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Determination of unknown photographic processing solutions through buffer curve analysis

Richard Winslow

DETERMINATION

OF

UNKNOWN PHOTOGRAPHIC PROCESSING SOLUTIONS

THROUGH

BUFFER CURVE ANALYSIS

by

Richard J. Winslow

A thesis submitted in partial fullfillment of the requirements for the degree of Bachelor of Science in the School of Photographic Science in the College of Graphic Arts and Photography of the Rochester Institute of Technology.

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ABSTRACT

The determination of photographic processing solutions through buffer curve analysis was investigated to determine its advantages, limitations, and general usefulness. A microprocessor controlled titration system was set up to perform up to 16 unassisted titrations and record the data on a floppy disk system at a speed five times faster than the speed of manual titrations.

The ingredients are not detectable by this analysis if their concentrations are much less than 1/10th the normality of the ingredient with the largest concentration that is detectable by this analysis. There is linearity between the concentration of a single ingredient solution and the volume of titrant required to reach the final endpoint, but this linearity fails when more than one ingredient is in the solution. This analysis is able to detect a significant number of ingredients used in photographic processing solutions. The analysis can be useful in analyzing competitors' products and photographic processor control.

INTRODUCTION

It was one of the objectives of the research to determine if an analysis of a photographic processing solution can be done through the use of acid-base titrations to determine the solution's ingredients and their concentrations. The acid-base titration is the measurement of the pH with the addition of an acid or base titrant to a solution. A buffer curve for a specific solution is the curve produced when the pH is plotted as a function of the volume of titrant added to the solution. The buffer curve can be expressed as the solution's resistance to a changing pH as an acid or base is added.

The ingredients in the solution, the ingredients' concentrations, and the volume of titrant are all factors that affect the buffer curve. The ingredients in the solution have specific values for equilibrium constants and a specific number of equilibrium constants which affect the buffer curve. A change in the values of equilibrium constants, the number of equilibrium constants, and/or the concentrations of the ingredients, will change the relationship between the pH and the volume of titrant. However, this change may not be large enough to be detected with the experimental resolution of the acid-base titrant.

This relationship is not unique for all ingredients at all concentrations. A specific combination of ingredients and concentrations of these ingredients may produce a buffer curve that is identical to another combination of ingredients and the concentrations of these ingredients. However, since only those chemicals with a specific purpose in a photographic processing solution will be analyzed, there exists a lower probability that the buffer curves

of these chemicals can be similiar.

At Versa Chem Corporation[1], this method of analysis has been used for several years to determine the chemical composition of unknown photographic processing solutions. This method is based primarily upon matching the buffer curve of the unknown solution with the buffer curve of a known solution. If the concentrations of all of the ingredients in the known solution equals the unknown solution, then the solutions' buffer curves will match. The known solution is made from knowledge of solutions with a similiar purpose and data obtained from preliminary determinations with the unknown solution. Quantitative determinations of hydroquinone, metol, sodium sulfite, and sodium thiosulfate and qualitative determinations for sodium carbonate, phenidone, and acetic acid may be included in the preliminary determinations. As an approximation of the unknown solution, the known solution's buffer curve is visually compared with the unknown solution's buffer curve. New approximations are made by visual extrapolation of the buffer curves until the known solution's buffer curve visually matches the unknown solution's buffer curve. Each new approximation must be mixed in the laboratory to obtain its buffer curve for comparison with the unknown solution's curve. After a match has been decided, other characteristics are considered, such as solution color, specific gravity, smell, and photographic performance.

The amount of time and materials used in this present method is

[1]Versa Chem Corporation, Box 116, Port Ewen, New York 12466

wasteful for two reasons:

First, the laboratory work involves a lot of unnecessary repetition. The known solutions' buffer curves are only used once for a specific unknown solution. Unknown solutions of one purpose in photography contain ingredients found in other unknown solutions with different purposes such as preservatives and buffers. If the data from these known solution buffer curves could be stored, then the repetition of laboratory work could be virtually eliminated to save time and materials.

Secondly, the present method uses the visual extrapolation to make new approximations for the concentrations of ingredients and visual comparisons to decide when a match has been achieved between the known solution's buffer curve and the unknown solution's curve. The visual extrapolation creates a lot of laboratory work as the approximations slowly closes in until a visual match is obtained. The visual matching also contributes to the error in the determination.

It was the purpose of this project to determine the usefulness of this method of analysis and offer improvements to the procedures used at Versa Chem Corporation. The resolution and limitations of this analysis were investigated to determine its usefulness and as the process was improved the same parameters were monitored. The improvements significantly saved time, saved materials, and systemized the process of analysis through computerization of the process' control. With a microprocessor coupled to the laboratory's titration equipment, the microprocessors control the operation of the titration equipment, the collection and storage of the data, and the manipulation

of the data. Data manipulation includes computer programs to list the results, to plot the data, to do a statistical analysis, or any computer program that can use the data.

There are many advantages to fitting a data set to a mathematical model. Fitting the buffer curve data sets to a mathematical model, which would represent the pH as a function of the ingredient concentrations and the volume of titrant, would have the following advantages. Equation fitting would only require a small number of laboratory generated buffer curves to produce an equation which would represent a buffer curve at any concentration of the ingredients in the equation. This would save laboratory time and materials. Only the equation would have to be stored in the computer instead of all the data points. The equations could also allow the use of statistical analysis. The project investigated the considerations involved in expressing the buffer curve with a mathematical model.

EXPERIMENTAL

I. Setting Up the Automatic Titrator

a) Interface to the 8008 microprocessor and improvements to increase the titrator's speed

Before data collection could begin, a laboratory was established to enable the mixing and the titrating of samples. An Intel 8008 microprocessor was set up to control the components of a titrator and collect the data. The following titrator components were interfaced to the microprocessor:

pH meter (Analytical Measurements) with a combination electrode (Broadley-James Corp., Model 9008)

Digital thermometer (Doric Scientific)

Digital clock

Titrant pump (Gorman-Rupp) that can deliver 0.5 ml/pump.

Moveable arm on a cam that lowers the probes and titrant hose into the sample beaker.

Turntable motor (Bodine gear reduction motor) to rotate the sample turntable.

Light probe and photo cell (Skan-O-Matic) to detect when a beaker is directly under the probes.

Magnetic Mixer (Troemner Corp., Model 500)

Each component was interfaced to the computer and a subroutine was created to control the component. With each component independently operative, an algorithm was created to sychronize all of the components to titrate up to 28 samples sequentially (See Figure 1).

With the time per titration significantly large, the algorithm had to be streamlined. Initially, there were three wash baths and a beaker of cotton to clean the probes after each titration. The

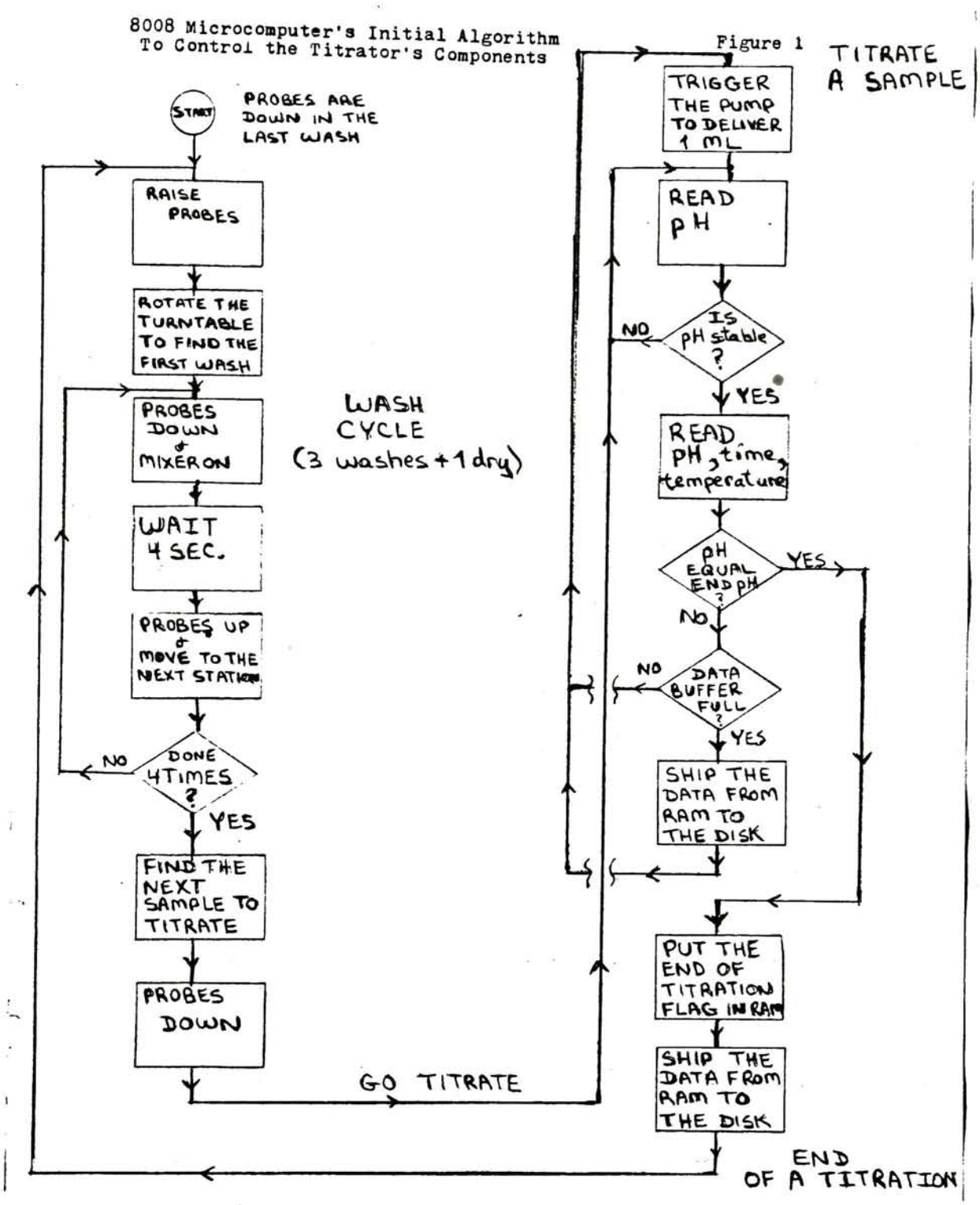

Fig. 1 8008 Microcomputer's Initial Algorithm to Control the Titrator's Components

wash baths and blotter were at the arbitrary station zero of the 32 station turntable. After each titration, the turntable had to rotate to the wash baths, wash the probes, and rotate to the next sample. This required two minutes for one full revolution of the turntable and 1 minute for washing. To save time without losing cleaning efficiency, each sample is now followed by a wash bath. The titrator can titrate a sample, move one station to wash the probes, and one more station to the next sample.

The algorithm had to detect a stable pH after each addition of titrant before storing the pH value that corresponds to that addition of titrant. Originally, the algorithm detected stability in the following manner. The computer read the pH, waited 6 seconds, and reread the pH. If the pH values were equal then the value was recorded and titrant was added to the solution. If the readings were not equal, the computer would go back and reread the pH until the pH could remain stable for 6 seconds.

To save time, this detection of pH stability was replaced by the following sequence. The pH is read every 2 seconds and compared to see if the pH values are within 0.01 of each other. If so the current value is stored and another addition of titrant occurs. If the pH readings are not stable within 0.01 pH units for 2 seconds, the readings continue until stability is detected.

The computer was originally storing the time, the solution's temperature and pH, and the volume of titrant for each addition of titrant. To save time, computer storage, and to simplify the algorithm, only the pH is being stored after each addition of titrant. There is a starting and finishing time and solution temperature

8008 Microcomputer's Improved Algorithm
To Control the Titrator's Components

Figure 2

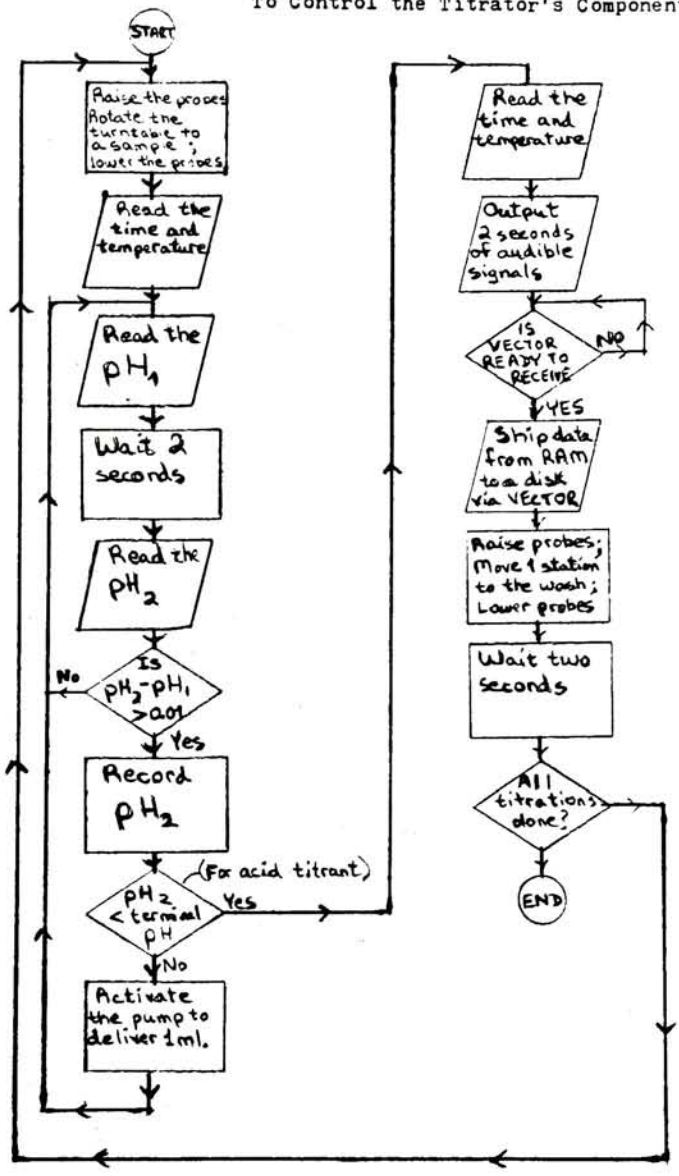

Fig. 2 8008 Microcomputer's Improved Algorithm to Control the Titrator's Components.

recorded at the beginning and the end of each titration. The volume of titrant is implied to start at zero and increment by one milliliter for each addition of titrant. The pH is recorded before the titrant is added to the solution until the terminal pH has been exceeded.

The final enhancement to the algorithm was to streamline the program to use the fastest instructions. The final algorithm is shown in Figure 2.

b) Interface to the Vector microprocessor and the utilization of the Vector I system

To permanently store the collected data, it had to be shipped over to a microprocessor called Vector I, which has two floppy disk drives to store this data. Interface software and hardware were created to efficiently transfer data between computers. As a good programming technique, the data was shipped from the 8008's temporary memory to a floppy disk after every titration. Thus only one titration's data set would be lost in the event of equipment failure.

The Vector computer is used to store the data on the permanent storage devices and to run the data manipulation programs. Manipulation programs were written to list the raw data values and to plot the buffer curves on a line printer or a CRT. Prewritten programs were put up on the Vector system for statistical correlation, multi-function curve fitting, and polynomial curve fitting. Thus, the computers can perform the titrations, collect and store the data, and manipulate the data. A diagram of the equipment interfaced to the microprocessors is shown in Figure 3.

Equipment Interfade Diagram
For the Automatic Titrator

Figure 3

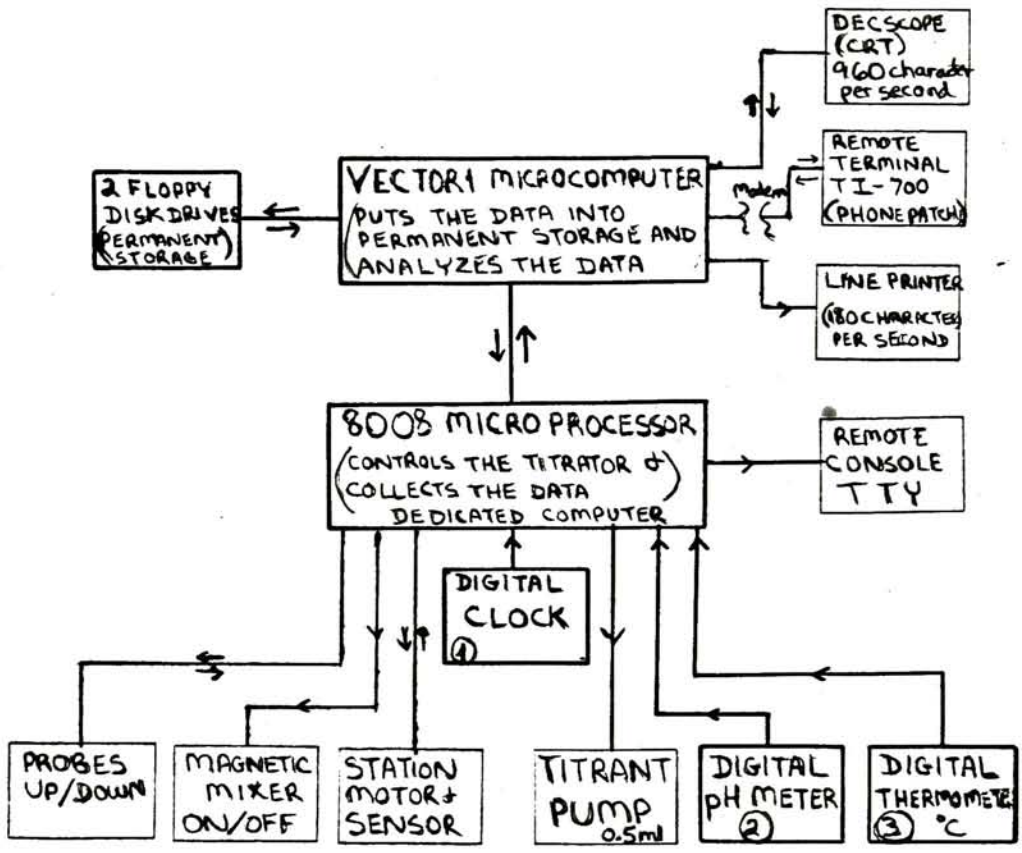

Fig. 3 Equipment Interface Diagram for the Automatic Titrator

c) The automatic titrator's standard operating procedures

The following standard operating procedures are used for doing titrations with the computer-controlled titrator. One milliliter samples are added to 75 mls. of deionized water and placed on the titrator turntable. Each sample is followed by a wash bath, which is a beaker of 150 ml. of deionized water. The standard data collection file is initialized on the Vector I computer by entering a heading which contains the permanent storage file name, the date, a description of the experiment, the titrant and its concentration, the number

```
            3/5/78    ACTIVA5.DAT
                                          Sample of a Titration's Data File Heading and a Plot of the Data
                2
               2   FACTORIAL EXPERIMENT                  4 SAMPLES ARE REQUIRED

INGREDIENT #  1:       SODIUM SULFITE
INGREDIENT #  2:     SODIUM HYDROXIDE
INGREDIENT #

ACID TITRANT

INGREDIENT -            SODIUM SULFITE     SODIUM HYDROXIDE
BEAKER #  1                   50.0               50.0
BEAKER #  2                   60.0               50.0
BEAKER #  3                   50.0               60.0
BEAKER #  4                   60.0               60.0

BE SURE TO:

1) SET THE CLOCK
2) CALIBRATE  THE PH METER
3) FILL THE TITRANT RESEVOIR

TOTAL NUMBER OF CURVES TO BE PLOTTED? 5

NUMBER OF CURVES LEFT TO BE READ: 5
NUMBER OF CURVES READ: 0
A SOURCE FILE? ACTVCC.DAT
STARTING CURVE AND # OF CURVES TO BE READ IN THIS FILE? 1,1
ACTVCC.DAT

3/4/78

ACID

1 1
UNKNOWN
.0
NUMBER OF CURVES LEFT TO BE READ: 4
NUMBER OF CURVES READ: 1
A SOURCE FILE? [redacted]DATA.FIL
STARTING CURVE AND # OF CURVES TO BE READ IN THIS FILE? 1,4
ACTIVA5.DAT

3/5/78

ACID

2 2
SODIUM SULFITE
50.0
60.0
SODIUM HYDROXIDE
50.0
60.0
```

KNOWN BUFFER CURVES

UNKNOWN BUFFER CURVE

Fig. 4a Sample of a Titration's Data File Heading

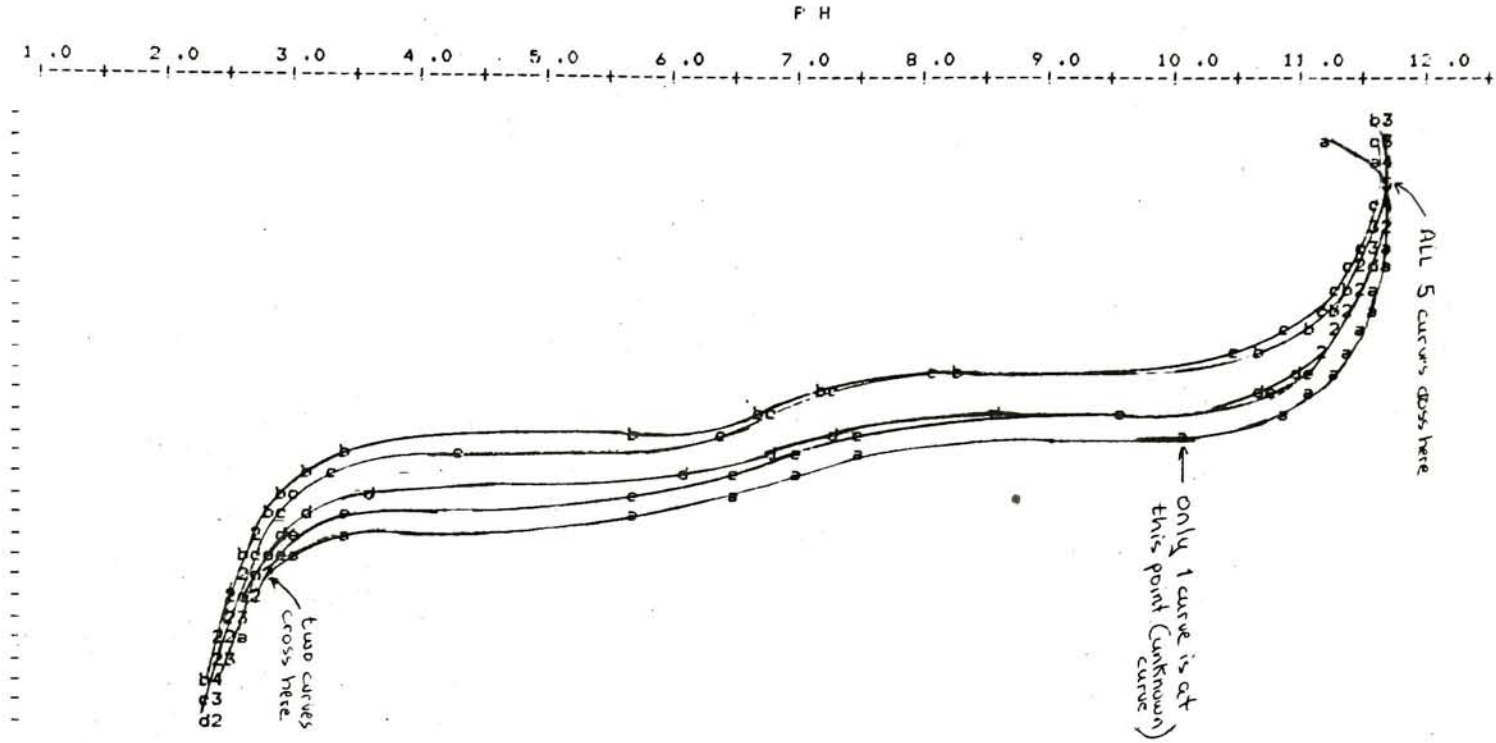

Fig. 4b A Sample Line Printer Plot of Buffer Curves.

of samples being run, and the ingredients and their concentrations. A sample data collection file heading is shown in Figure 4a. The titrator control program on the 8008 computer is then started. A sketch of the titrator is shown in Figure 5. Under the control of this microprocessor, the equipment operates in the following manner. The probes are raised out of a wash bath and the turntable is rotated to the first station; the probes are lowered into this first sample; the magnetic mixer is turned on; the initial time and solution temperature are read and stored in temporary memory. The algorithm waits for the pH to stabilize within 0.01 pH units for more than 2 seconds. When a stable pH is detected, the reading is stored in temporary memory and the titrant pump is activated twice to deliver

Figure 5

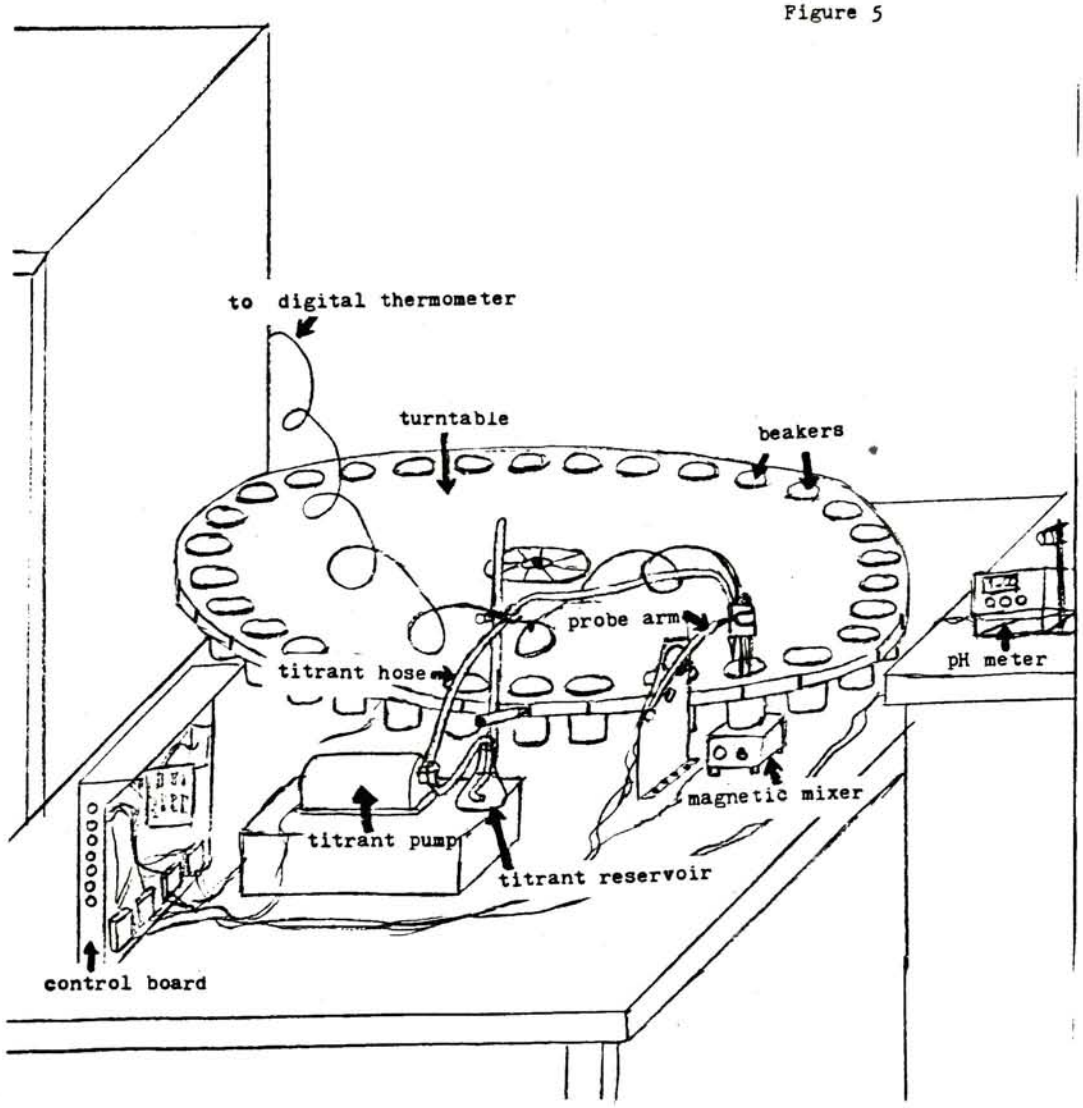

Fig. 5 Sketch of the Automatic Titrator's Components and Layout

one milliliter of titrant to the sample. This stable pH detection and titrant addition continues until the pH exceeds a predetermined pH. At this time the 8008 computer sends out 2 seconds of audible signals to alert the operator that the 8008 microprocessor is waiting to transfer data to permanent storage via the Vector I system. When the communication program is running on the Vector computer, the data can be transferred from the 8008's temporary

memory to the floppy disk storage. After all of the data for the one titration has been transferred, the 8008 computer continues by raising the probes, moving one station to a wash bath, and lowering the probes into the wash bath. After 2 seconds in the wash bath, the probes are again raised, the turntable is moved one station, the probes are lowered, and the next sample's titration begins. The process continues until all the samples on the turntable are titrated. When the two microprocessors are dedicated to the titrator, the system can perform up to 16 unassisted titrations.

II. Testing the Automatic Titrator's Environment and Equipment

When the titrator was functional, tests were run to evaluate the titrator's operation. A solution's temperature and the pH meter amplifier were monitored for a 12 and 21 hour period. The thermometer probe was immersed in 100 mls. of water and the pH probe was removed from the amplifier to eliminate variability due to the probe. The pH meter amplifier value, the temperature, and the time were recorded every 15 minutes for these two time periods. These tests were to evaluate temperature changes and pH meter drift as a function of time (See Graphs 1 and 2 on pp. 26-27).

The accuracy of the titrant pump was investigated under a number of conditions. The accuracy was measured by activating the pump ten times to deliver an expected volume of 5 mls. into a 5 ml. buret. The different conditions are as follows:

The pump's delivery tip was suspended above the buret; the delivery tip was touching the buret; the pump was primed once prior to measurement; a specific time lag was imposed between tests; and

the titrant reservoir, the pump, and the pump delivery tip were placed at the same height. The outcome of these tests are tabulated on p. 24.

The titration process requires a 1 milliliter sample to be added to 75 mls. of deionized water in a 200 ml. beaker to insure that the probes are sufficiently immersed. To measure the effect that the volume of water had on the pH of the solution, titrations were performed with 60, 80, and 100 mls. of water with 1 ml. of an activator (See Graph 3 on p. 28).

The standard error of the automatic titrator was measured as follows. A 5 ml. sample of activator was mixed with 375 mls. of deionized water to make five titration samples that would not be influenced by error due to the mixing of samples. The five samples were submitted as one run. The experimental error was measured by calculating the variability at each volume of titrant. The following formula was used to determine the standard error.

$$\sigma_e = \frac{\sum(x_{ij} - \bar{x}_i)^2}{r(c - 1)}$$

where $r = i$ = levels of pH
$c = j$ = replicate buffer curves

The standard error of the manual titrations was measured on the equipment at Rochester Institute of Technology. This was done by titrating three 0.5 ml. samples of D-76 developer and three 0.5 ml. samples of D-72 developer. In a similiar manner, the error was measured by computing the variability at each volume of titrant. The values of the standard error for the automatic titrator and the manual titration have been tabulated on p. 24. The variability of the automatic titrator and the manual titrations were compared along with other factors such as time per titration, the operator's work

that is required per titration, and the type of data storage being used be each titrating method.

III. Setting up a Laboratory to Perform Manual Titrations

a) Organization of the equipment

With the limited access to the automatic titrator, a manual titration process had to be set up at Rochester Institute of Technology. A 100 ml. graduated cylinder is used to measure the 75 ml. ± 1 ml. volume of distilled water; five milliliter burets are used to deliver the samples; a 50 ml. buret is used to deliver a titrant to the sample; a magnetic mixer is used to disperse the additions of titrant; a Corning research pH meter (RIT #62632) with a combination electrode measures the pH; and a pH 9.00 buffer is used to calibrate the pH meter. All of the glassware was thoroughly washed with Alconox and the pH meter was calibrated.

After the titration equipment was organized, an acid and a base titrant had to be mixed and standardized. Six liters of each titrant and one liter of 0.100 N sodium hydroxide Acculute[2] were mixed. The sodium hydroxide Acculute solution was used to standardize the sulfuric acid titrant (See Figure 6). The standardization was done by titrating the Acculute solution into 10 mls. of the sulfuric acid. The standardized sulfuric acid titrant was then used to standardize the base titrant by titrating the standardize sulfuric acid into 10 mls. of unstandardized sodium hydroxide titrant. The buffer curves were plotted and the endpoints were used to find the normality of

[2]Acculute is concentrated volume that has been accurately prepared to give a standardized solution when diluted to its specified volume.

Flowchart of the Titrant Standardization Figure 6

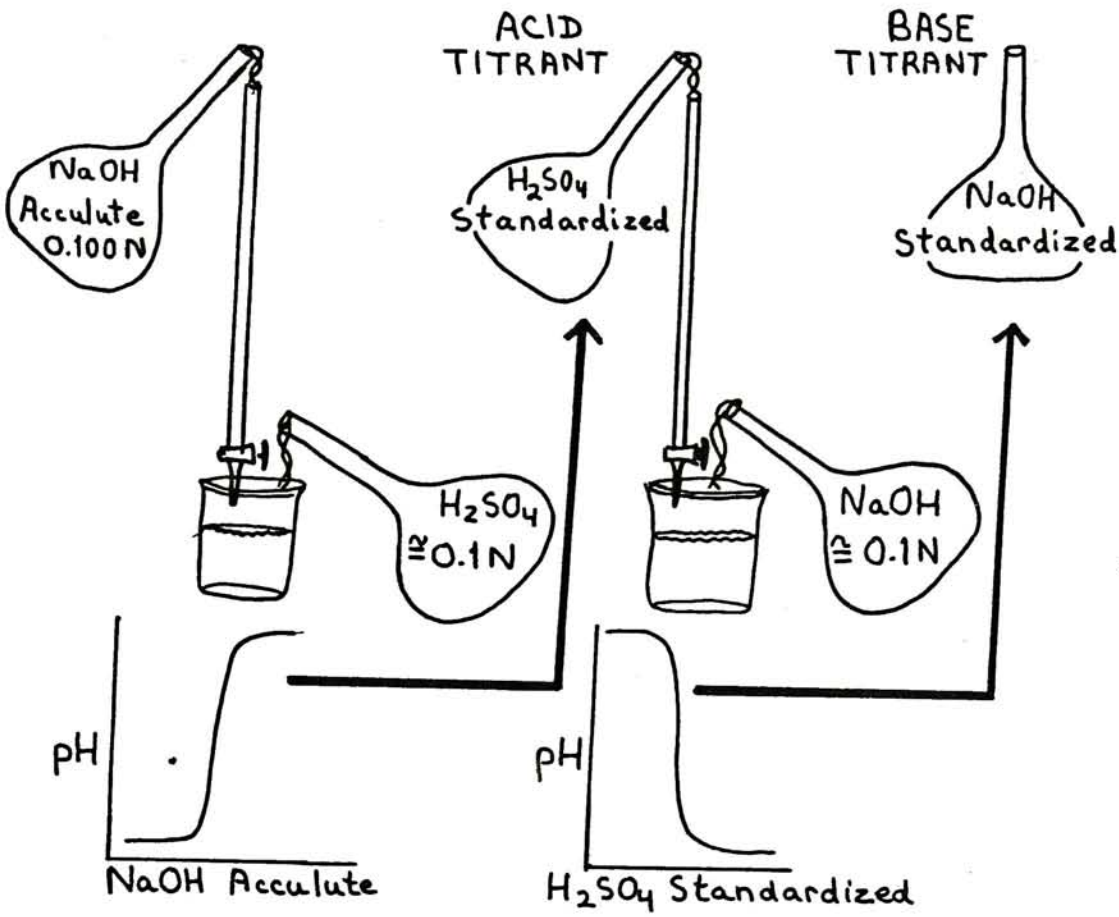

Fig. 6 Flowchart of the Titrant Standardization

the titrants. The buffer curves are shown in Graph 22 on p. 49 and the normality for each titrant is given on p. 24.

b) Standard operating procedures for the manual titrations

The standard operating procedures for the manual titrations done at the Institute are described below. Concentrated solutions of the ingredients that make up the known samples are put into the 5 ml. burets. A 250 ml. beaker is filled with 75 ± 1 ml. of distilled water and a magnetic stirring bar is added. Volumes of each ingredient

are added to the beaker to make the equivalent of a 1 ml. sample of a photographic processing solution at a stock dilution. If an unknown solution is being titrated, one milliliter is measured into the beaker of distilled water.

The pH meter is standardized to the pH 9.00 buffer; the sample is placed on the magnetic stirrer; the stirrer is started; the pH probe is lowered; and the titrant buret is filled and centered over the beaker. When the sample's pH is stable to 0.01 pH units, the reading is recorded in tabular form and on a graph. The graph is used to determine the volume of titrant to add, depending on how close the pH is to an endpoint. The 50 ml. buret is then used to deliver the predetermined volume of titrant and the pH is again allowed to stabilize. This process continues until a preset termination pH has been exceeded. At this time, the mixer is turned off; the pH meter put on standby; the probe is raised and rinsed with distilled water into the finished sample. The beaker is washed and a new titration may begin.

IV. Evaluating the Buffer Curve Analysis

a) Monitoring the stability of the concentrated sample solutions

The concentrated solutions are stored in 125 ml. erlenmeyer flasks with rubber stoppers. The initial storage volume, after the solutions are made, is such that only 2 mm of air space is allowed between the rubber stopper and the solution, but as the solution is used, the volume of air in the flask increases. As the experiments were carried out over a three week period, samples were repeated to determine if the solutions had been affected by time and

air. After three weeks, all fresh solutions were mixed and titrated within 24 hours to further measure the effects of air and time. These checks continued for the fresh solutions. The buffer curves for the fresh and old solutions can be compared in Graph 4 on p. 29.

b) Factorial Experiments

A number of two level factorial experiments were designed to include the combination of ingredients of photographic processing solutions. The concentrations of the ingredients were set to exceed the typical range of concentrations used in photographic processing solutions. Thus a typical range of 30 g/l to 100 g/l of sodium sulfite might have a concentration range of 10 g/l to 100 g/l in one of these factorial experiments.

A 2^3 factorial experiment was performed for the ingredients of an activator - sodium sulfite, sodium hydroxide, and Na_4EDTA (See Graph 5 on p. 30). From these results, a 4^2 factorial experiment was designed and carried out using sodium sulfite and sodium hydroxide (See Graph 6 on p. 31). To evaluate the ingredients of a concentrated developer, a 2^4 factorial experiment was designed with these ingredients - sodium sulfite, hydroquinone, potassium hydroxide, boric acid, and a constant level of ethylene glycol to allow the high concentration of hydroquinone to go into solution (See Graph 7 on p. 32). These factorial experiments were performed at Versa Chem Corporation with the automatic titration system.

With the manual titration system, two other factorials were designed. The first factorial included the ingredients found in Kodak's D-76 developer while the second factorial experiment

followed the constiuents of Kodak's D-72 developer. The buffer curves for these factorial experiments are illustrated by Graph 8 on p. 33 and Graph 9 on p. 34, respectively. Kodak's D-76 developer contains sodium sulfite, hydroquinone, elon, borax, and potassium bromide while Kodak's D-72 developer uses sodium carbonate as a buffer instead of borax. The ingredient concentrations had a range which is typically used for the purpose of a photographic developer.

c) Single ingredient concentration series

Single ingredient concentration series were also run for a number of ingredients found in photographic developers, activators, fixers, or stabilizers. These single ingredient titrations included aluminum sulfate, acetic acid, sodium sulfite, hydroquinone, elon, potassium bromide, boric acid, borax, sodium carbonate, sodium thiosulfate, and potassium alum (See Graphs 10-20 on pp. 35-47). Samples of D-76 and D-72 were also titrated and illustrated in Graph 21 on p. 48.

When the single ingredient concentration series for potassium bromide was evaluated, it was found that a change in the ingredient's concentration showed no significant change in the buffer curve with concentrations four times larger than would be use in photographic processing solutions. Further tests were carried out to see if potassium bromide changed the buffer curve with other ingredients present. This was done by titrating a 10 g/l solution of potassium bromide into a solution that contained 1 ml. of D-76 developer and 75 mls. of distilled water. After 20 mls. of the potassium bromide titrant were added, the resulting sample was titrated normally with 0.1005 N sulfuric acid. This buffer curve was compared with a buffer

curve for D-76 developer without any extra potassium bromide added. The results can be compared by referring to Graph 15b on p. 42.

d) Further evaluations

After analyzing the factorial experiments and single ingredient concentration series, those ingredients that could be significantly detected within the typical concentration of photographic processing solutions were chosen from the D-76 and D-72 developers. The exact concentrations of these significant ingredients were mixed and titrated to compare their buffer curves with the developer solutions made from Kodak (See Graph 4 on p. 29).

In order to obtain a larger pH range, samples of sodium sulfite had 10 ml. of sulfuric acid added to them after which they were titrated with the base titrant. Graph 12b illustrates the buffer curves with the extended pH. These buffer curves were compared to titrations without acid added, to determine if there is a distinct advantage to an increased pH range.

e) Mathematical representation of data

The relationship of a single ingredient's concentration to volume of titrant required to reach the final endpoint was plotted. From the linear plots, the slopes were determined for sodium sulfite, sodium carbonate, and the combination of the two at equal concentrations. These experimental slopes were compared to theoretical slopes calculated from the knowledge of the ingredient's molecular weight and the titrant's normality. The theoretical and actual calculations are tabulated on p. 24 and illustrated in Graph 23 on p. 50.

Using the assumption that acid and base titrants dissociated 100%, their theoretical relationships between pH and volume of titrant were calculated. The relationships were calculated for sodium hydroxide titrated with sulfuric acid and sulfuric acid titrated with sodium hydroxide. These relationships are written out on p. 25. The plots of these relationships were compared to the experimental results obtained when the titrants were standardized. This is illustrated in Graph 22 on p. 49.

The results from this research are designed to determine the feasibility of the analysis. In doing so, the possibilities for fitting the buffer curves to a mathematical model were investigated. A number of mathematical models were considered - linear regression through transformation, multicurve regression, the method of principal components, and the Simplex method of equation fitting.

RESULTS

Automatic Titrator Pump Accuracy

	$\bar{x}$	sd	n
Primed the pump once ; delivery tip touching buret -	5.033	0.023	3
No priming; delivery tip touching buret -	4.984	0.0434	11
Two minute time lag between tests; delivery tip suspended above buret -	4.947	0.0231	3
No time lag; delivery tip suspended -	4.998	0.0108	6
Delivery tip touching -	4.996	0.0440	14

Automatic Titrator Standard Error

Standard Error = 0.04850 n = 8 replicates of buffer curves

Time/titration = 16 min./35 ml. of titrant added (initial algorithm)
6 min./35 ml. of titrant added (final algorithm)

Manual Titration Standard Error

Standard Error = 0.06361 n = 6 replicates of buffer curves

Time/titration = 30 min./35 ml. of titrant added

Standardization Values for the Acid and Base Titrants

Acid Titrant - 0.1005 N sulfuric acid

Base Titrant - 0.0975 N sodium hydroxide (not used)
0.1000 N sodium hydroxide (Acculute, used for titrant)

Theoretical Calculations for Ingredient Concentration vs. Volume of Titrant

Sodium sulfite (g/l) = 126 g/mole x 1000 samples/liter x 1 mole/eq x 0.0001 eq/ml x Volume of Titrant (ml)

= 12.667 x Volume of Titrant (ml)

(Assumed 1 mole/eq because the pH started below the first endpoint)

Sodium carbonate (g/l) = 105.99 g/mole x 1000 samples/liter x 1 mole/2 eq x 0.0001 eq/ml x Volume of Titrant (ml)

= 5.326 x Volume of Titrant (ml)

Actual Calculations for Ingredient Concentration vs. Volume of Titrant

Sodium sulfite (g/l) = 14.8 x Volume of Titrant (ml)

Error = Actual slope/Theoretical Slope = 15%

Sodium carbonate (g/l) = 6.061 x Volume of Titrant (ml)

Error = 13.8%

Mathematical Model of Buffer Curve by Chemical Theory

Assumption: All ingredients dissociate 100%

Acid Titrant -

pH = 14 + log (equivalents of starting solution - milliliters of titrant x 1 liter/ 1000 ml x 0.1 equivalents/ liter)

Base Titrant -

pH = - log (equivalents of starting solution - milliliters of titrant x 1 liter/ 1000 ml x 0.1 equivalents/ liter)

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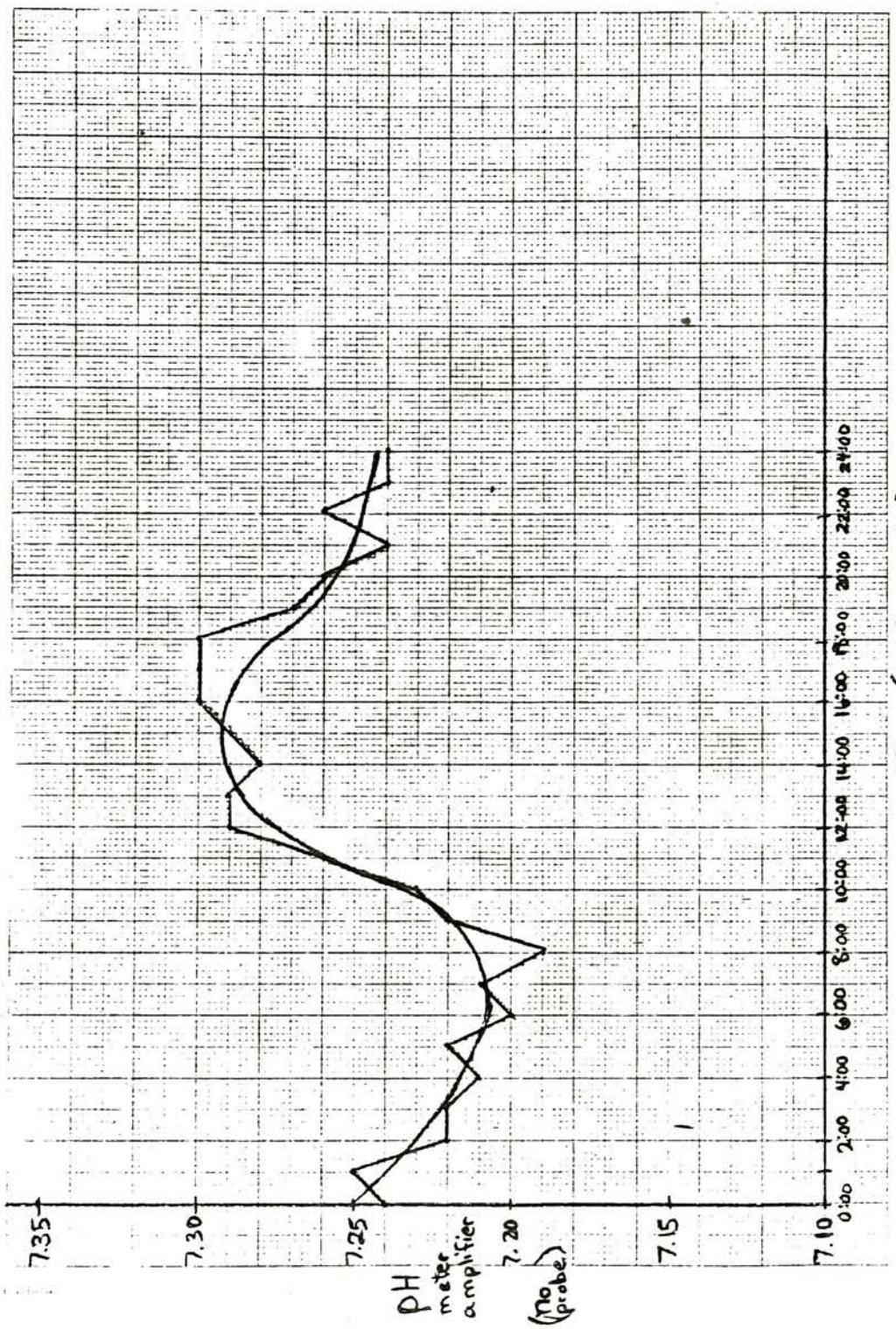
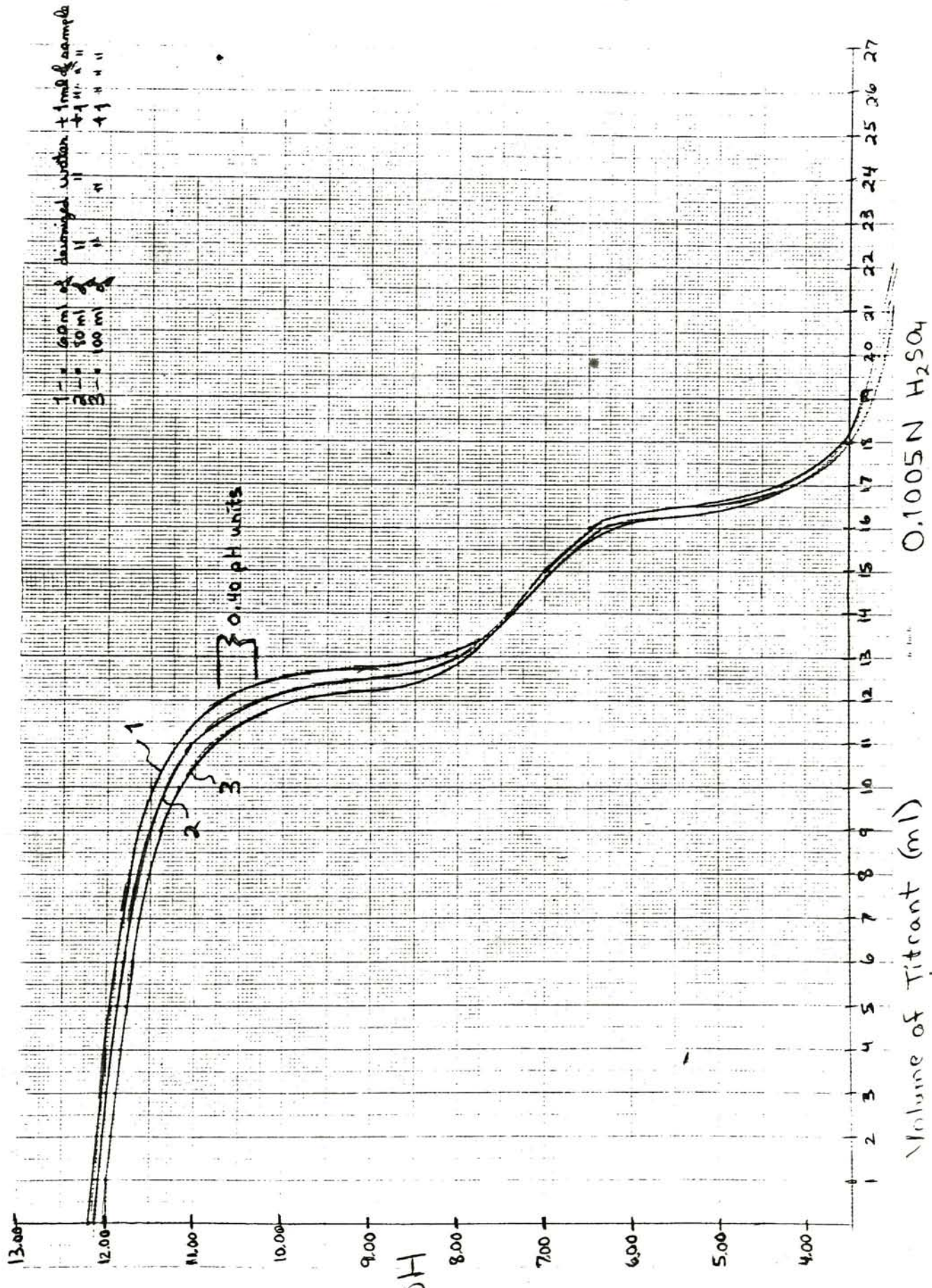
GRAPH 2

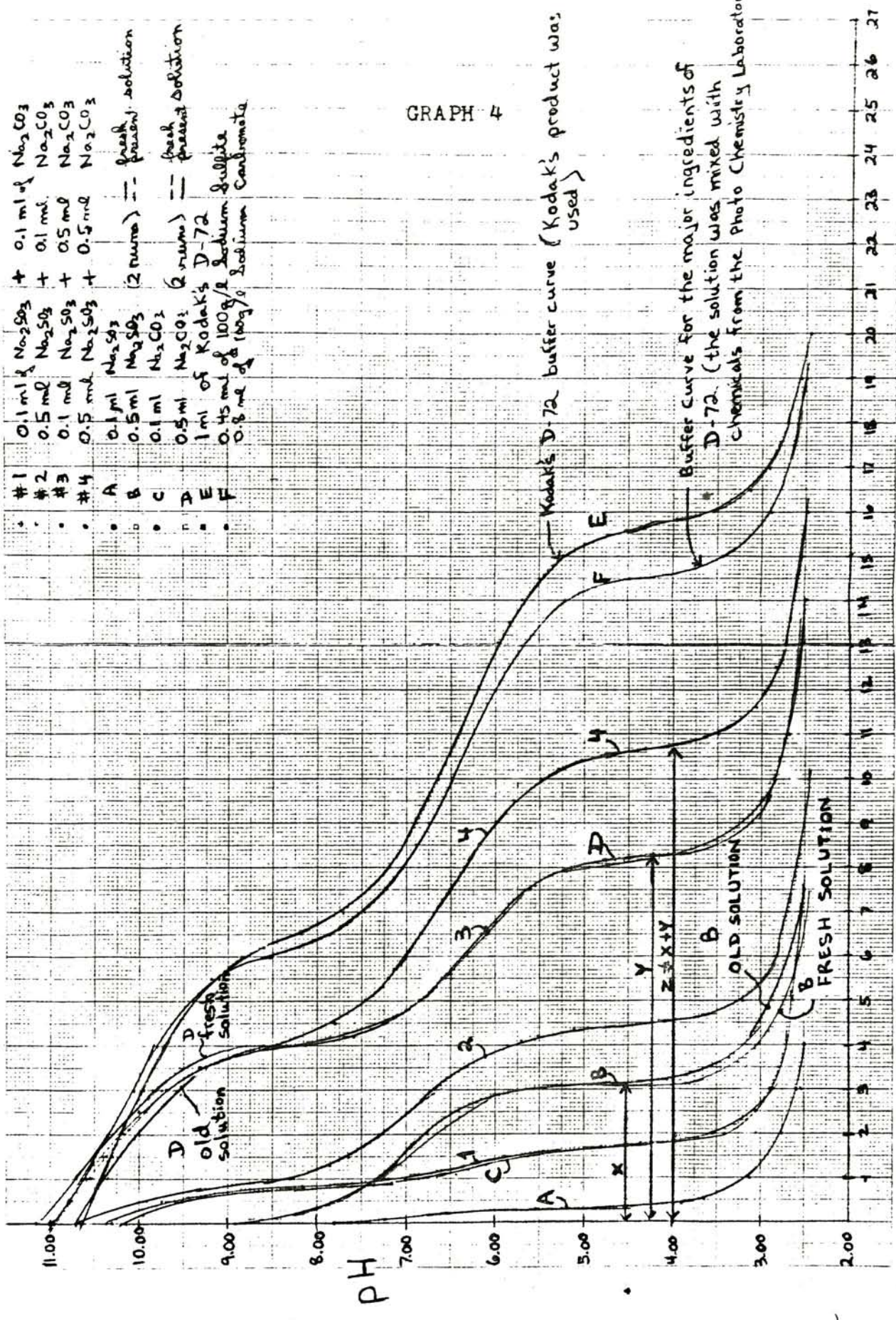
Digital pH Meter Amplifier vs. Time



GRAPH 3

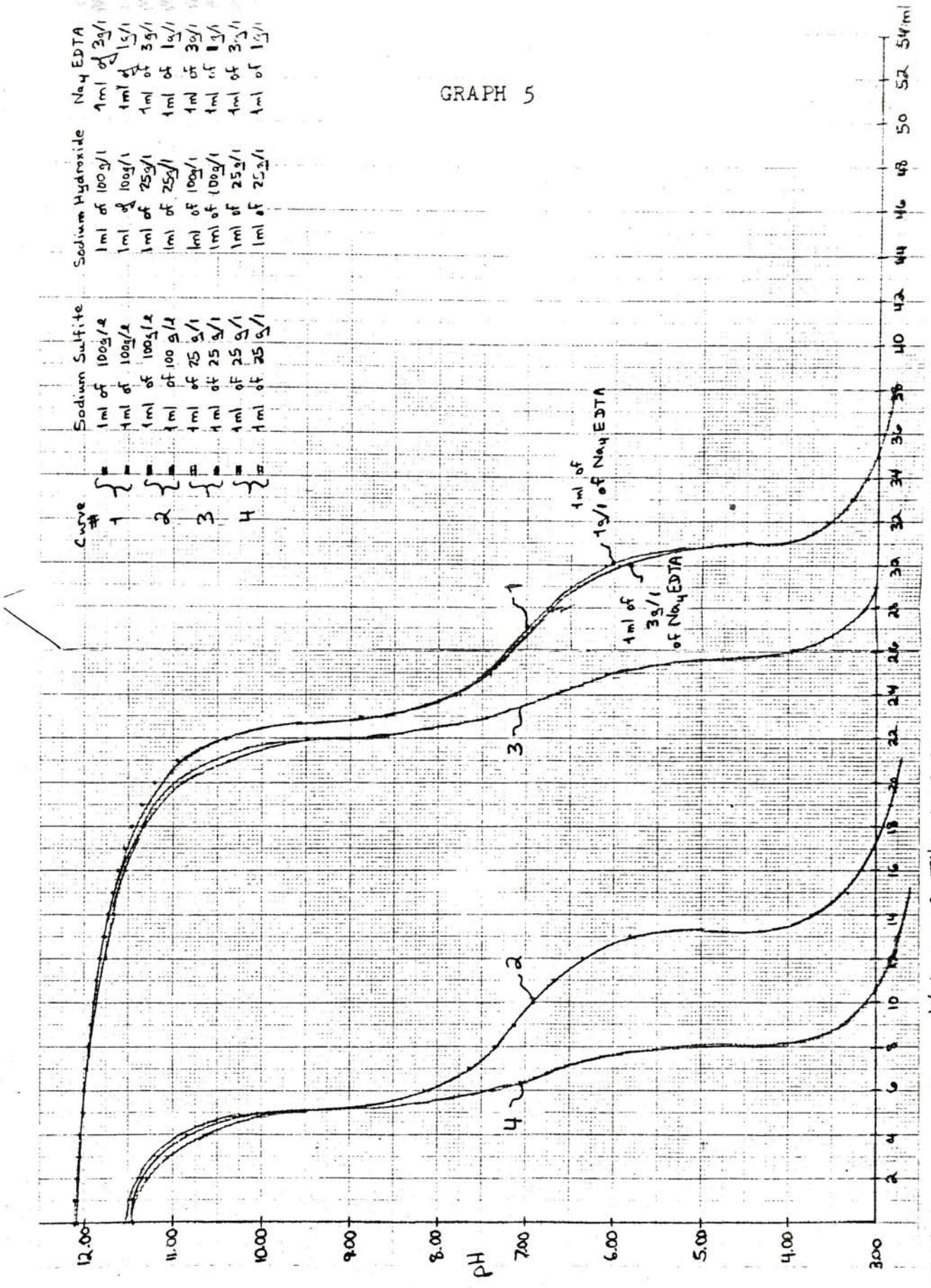
pH Dependence on the Initial Volume of Water





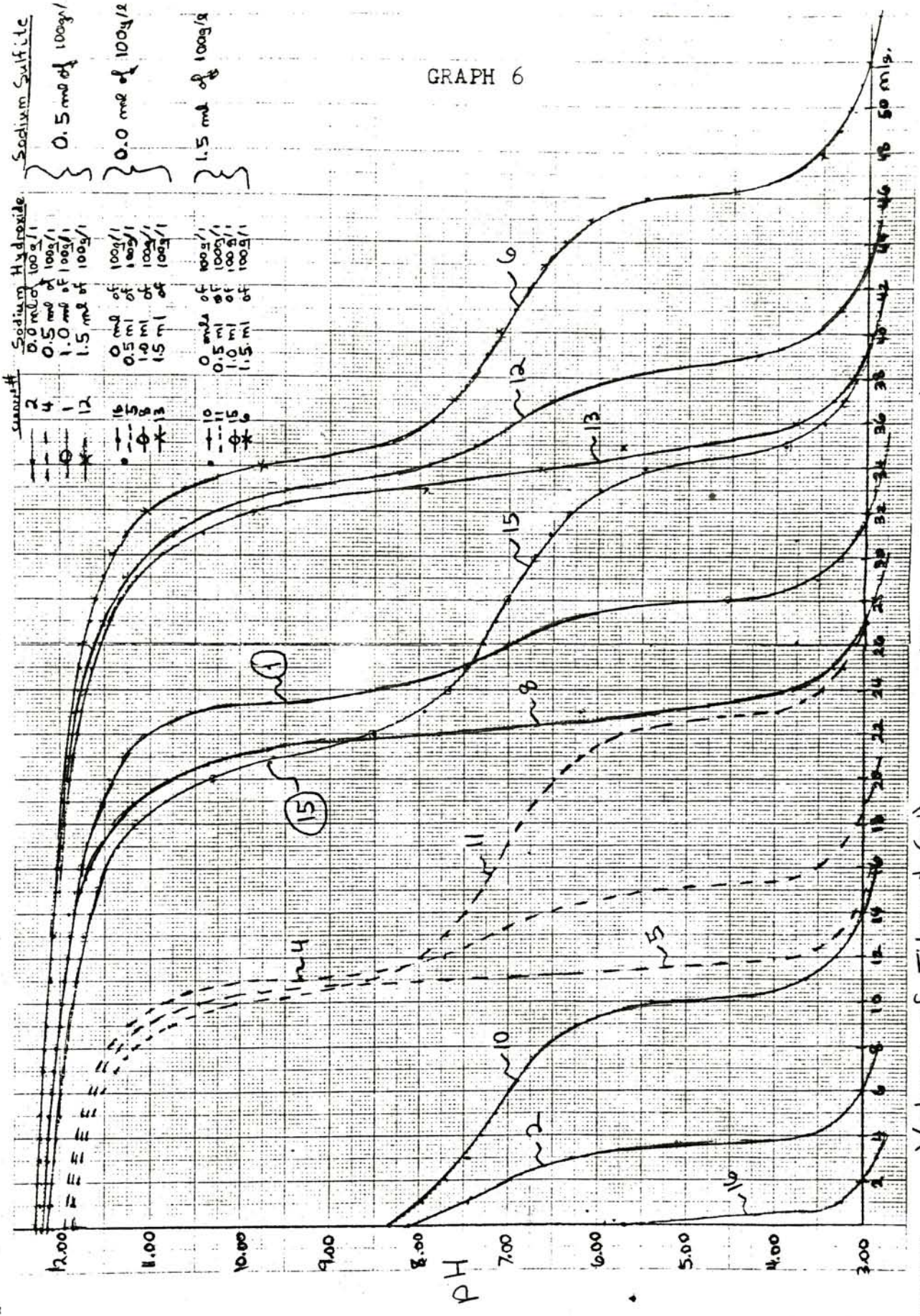
Sodium Sulfite and Sodium Carbonate -
Single and Double Ingredient Concentration Series

GRAPH 5



Sodium Sulfite, Sodium Hydroxide, and Ethylene Diamine Tetracetic Acid With 4 Moles of Sodium Ion - 2^3 Factorial Experiment

GRAPH 6

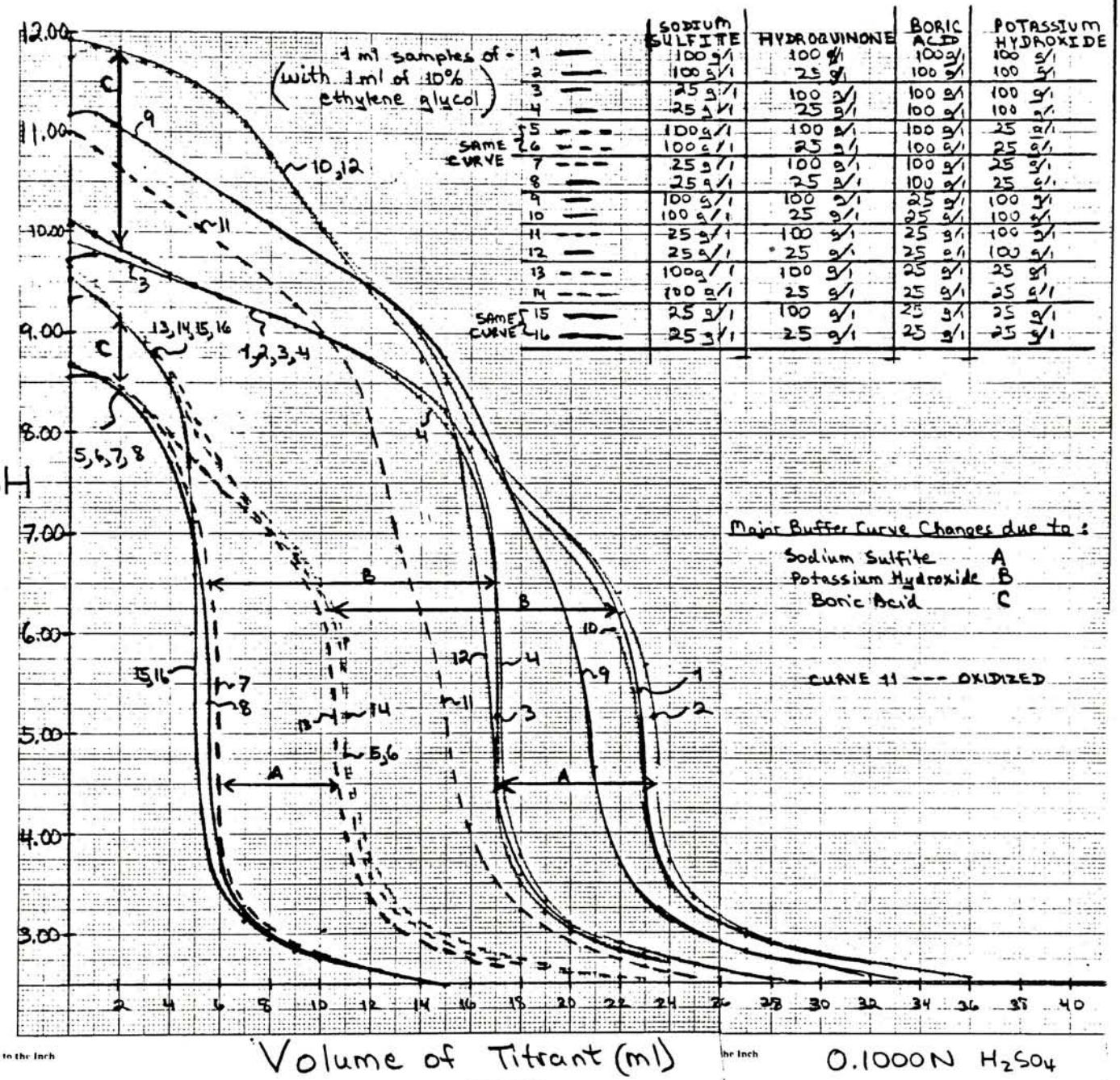


Sodium Sulfite and Sodium Hydroxide -
4^2 Factorial Experiment

GRAPH 7

Potassium Hydroxide, Hydroquinone, Sodium Sulfite, and Boric Acid with constant level of ethylene glycol -

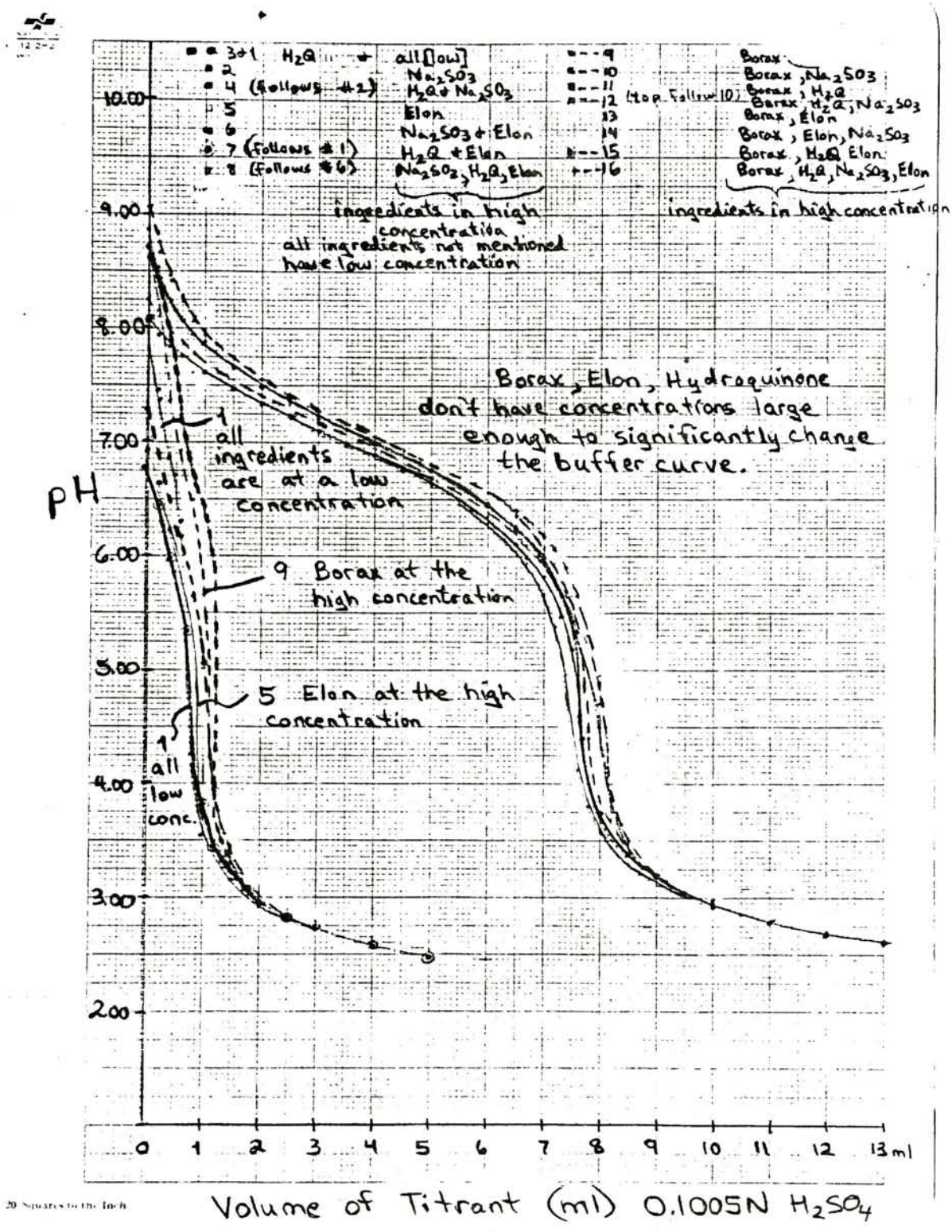
2^4 Factorial Experiment



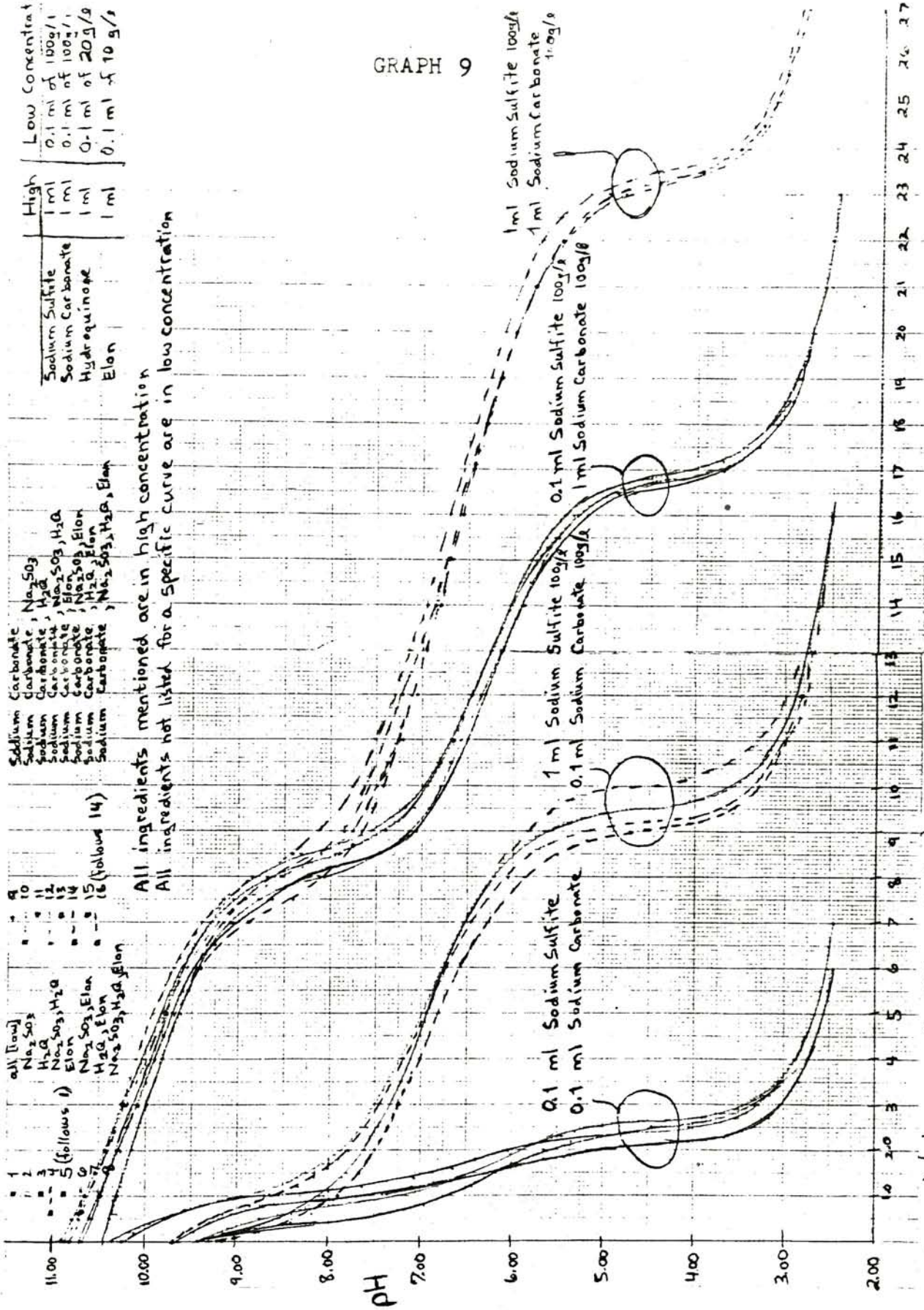
	Sodium Sulfite	Hydroquinone	Boric Acid	Potassium Hydroxide
1	100 g/l	100 g/l	100 g/l	100 g/l
2	100 g/l	25 g/l	100 g/l	100 g/l
3	25 g/l	100 g/l	100 g/l	100 g/l
4	25 g/l	25 g/l	100 g/l	100 g/l
5	100 g/l	100 g/l	100 g/l	25 g/l
6	100 g/l	25 g/l	100 g/l	25 g/l
7	25 g/l	100 g/l	100 g/l	25 g/l
8	25 g/l	25 g/l	100 g/l	25 g/l
9	100 g/l	100 g/l	25 g/l	100 g/l
10	100 g/l	25 g/l	25 g/l	100 g/l
11	25 g/l	100 g/l	25 g/l	100 g/l
12	25 g/l	25 g/l	25 g/l	100 g/l
13	100 g/l	100 g/l	25 g/l	25 g/l
14	100 g/l	25 g/l	25 g/l	25 g/l
15	25 g/l	100 g/l	25 g/l	25 g/l
16	25 g/l	25 g/l	25 g/l	25 g/l

GRAPH 8

Hydroquinone, Elon, Sodium Sulfite, and Borax - 2^4 Factorial Experiment



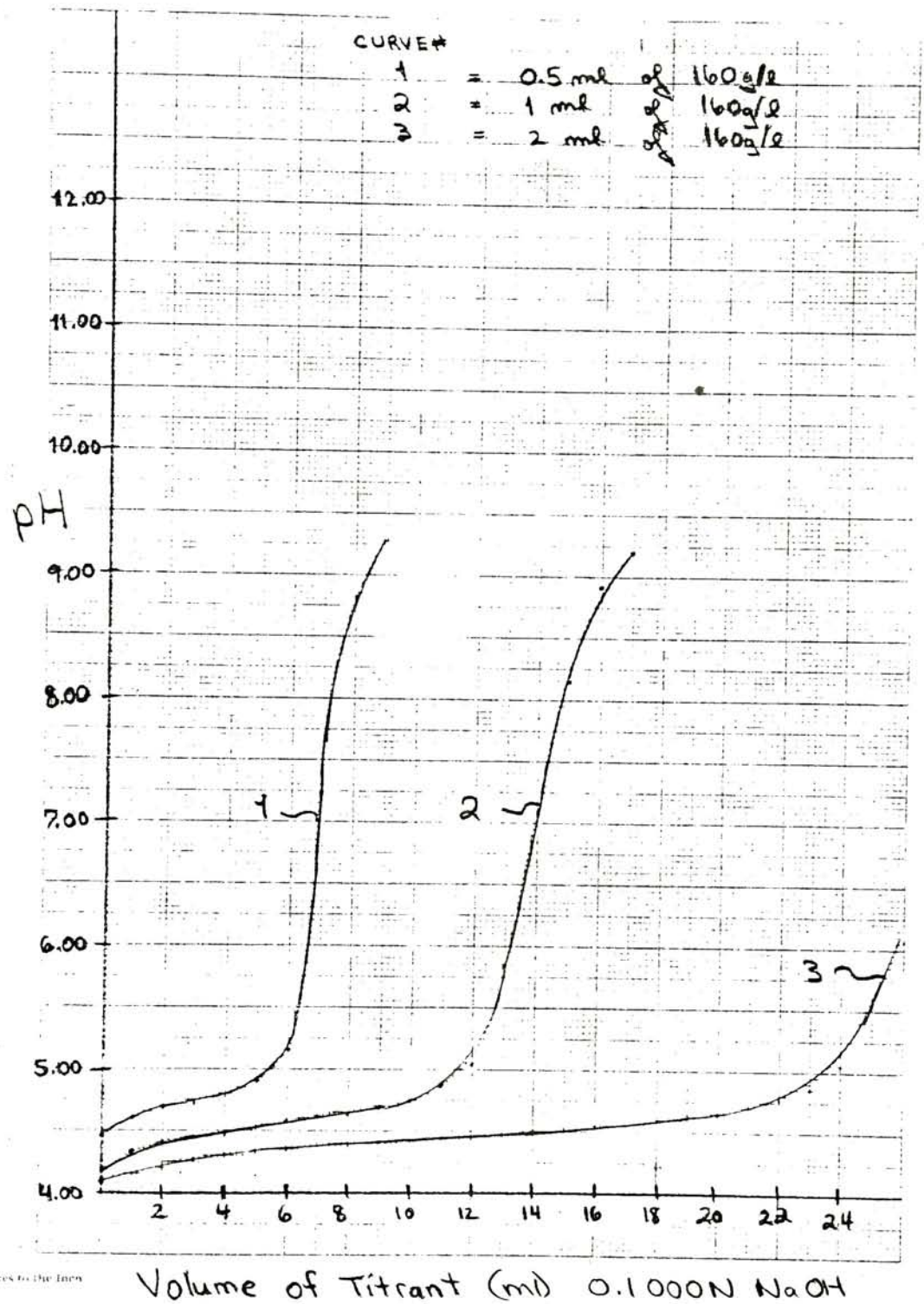
GRAPH 9



Hydroquinone, Elon, Sodium Sulfite, and Sodium Carbonate -)
2^4 Factorial Experiment

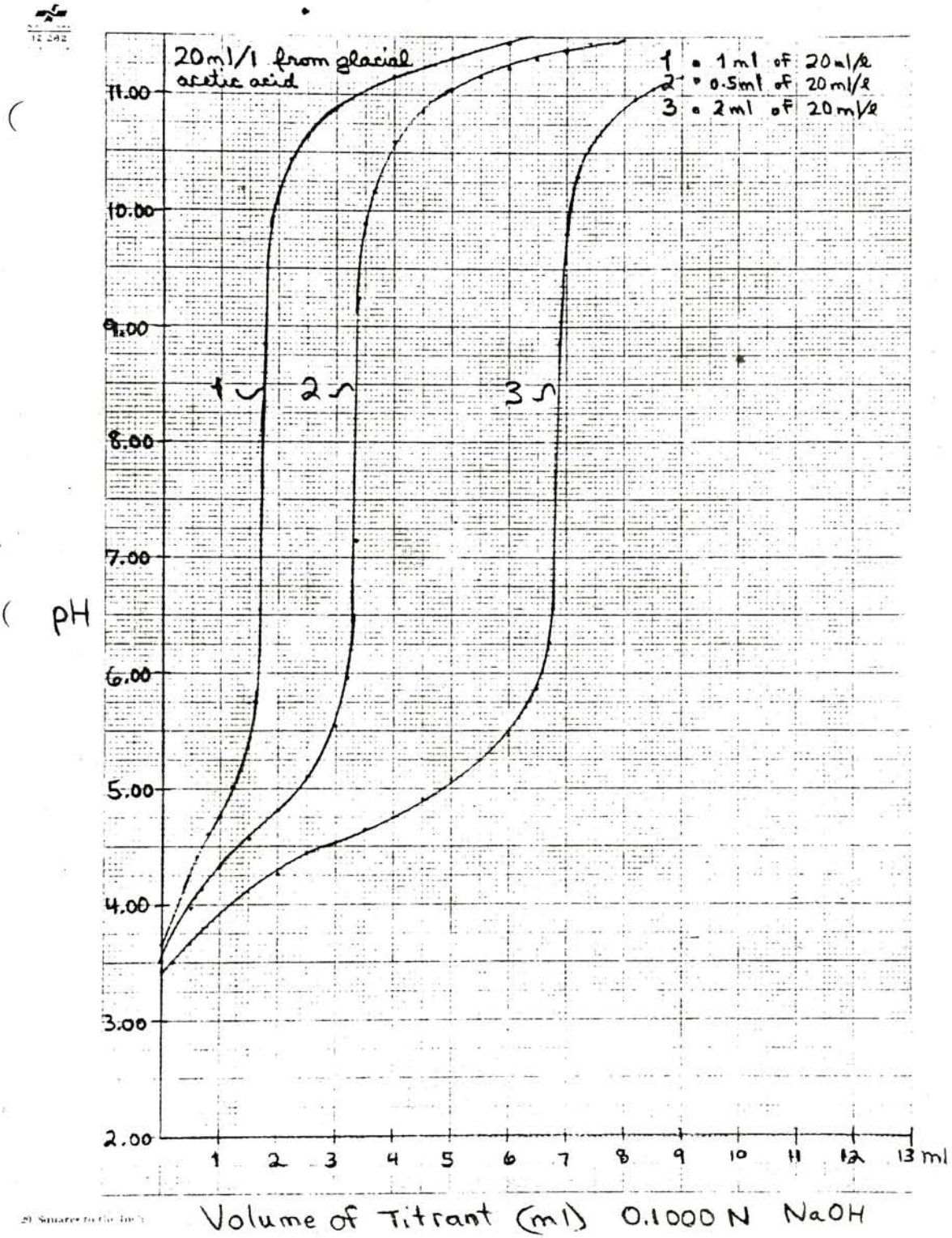
GRAPH 10

Aluminum Sulfate -
Single Ingredient Concentration Series Buffer Curves



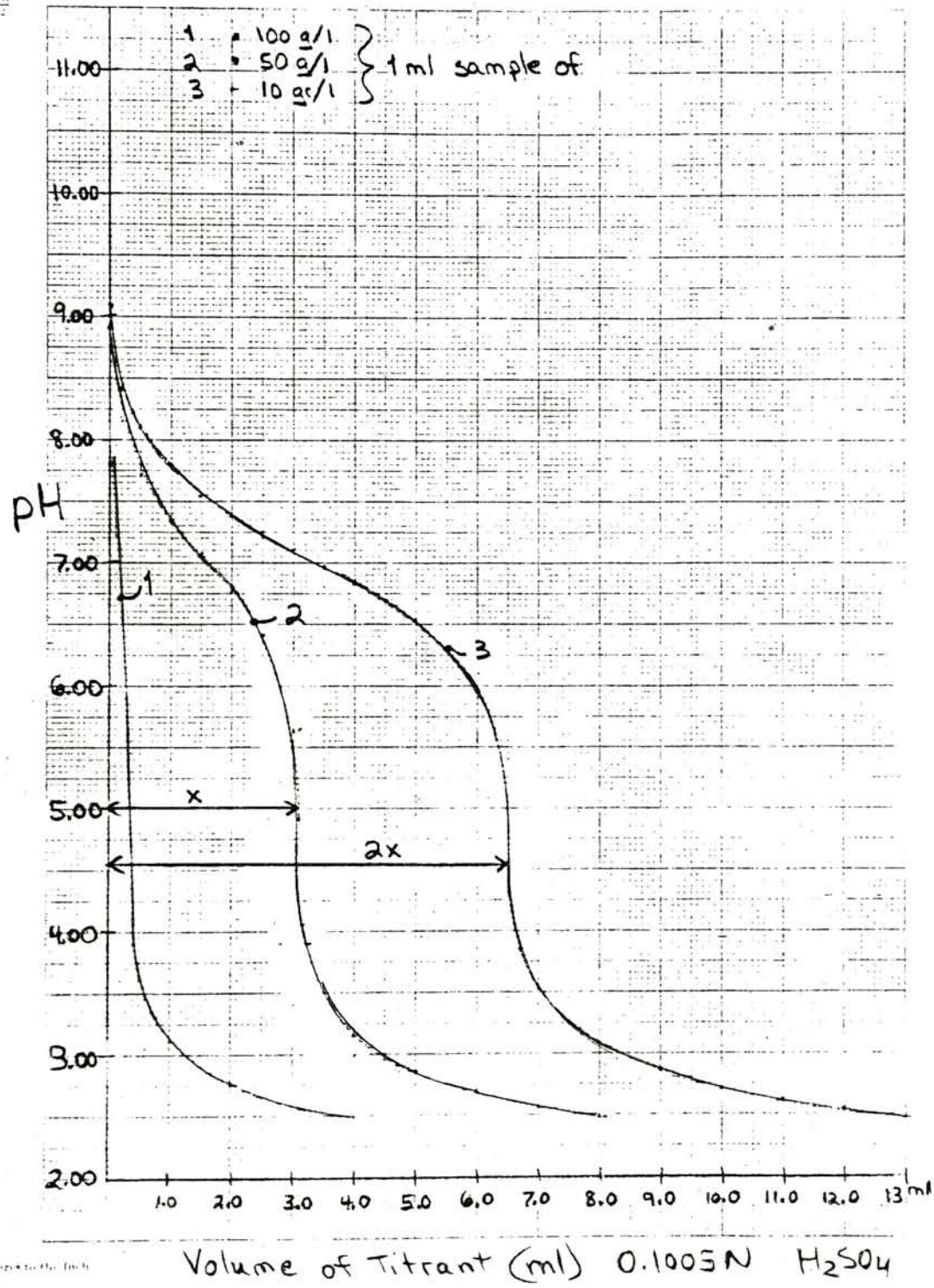
GRAPH 11

Acetic Acid -
Single Ingredient Concentration Series Buffer Curves



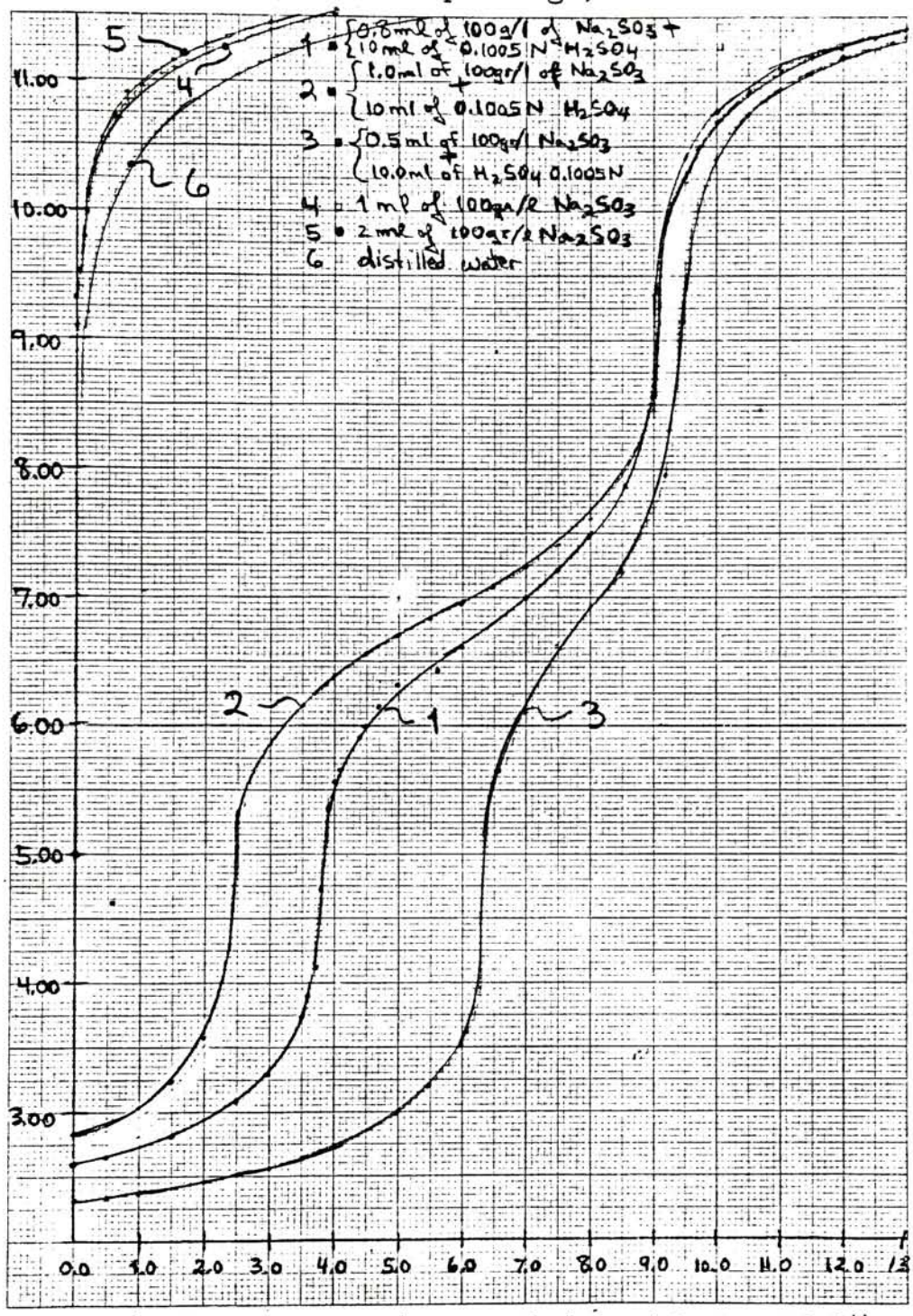
GRAPH 12a

Sodium Sulfite -
Single Ingredient Concentration Series Buffer Curves



GRAPH 12b

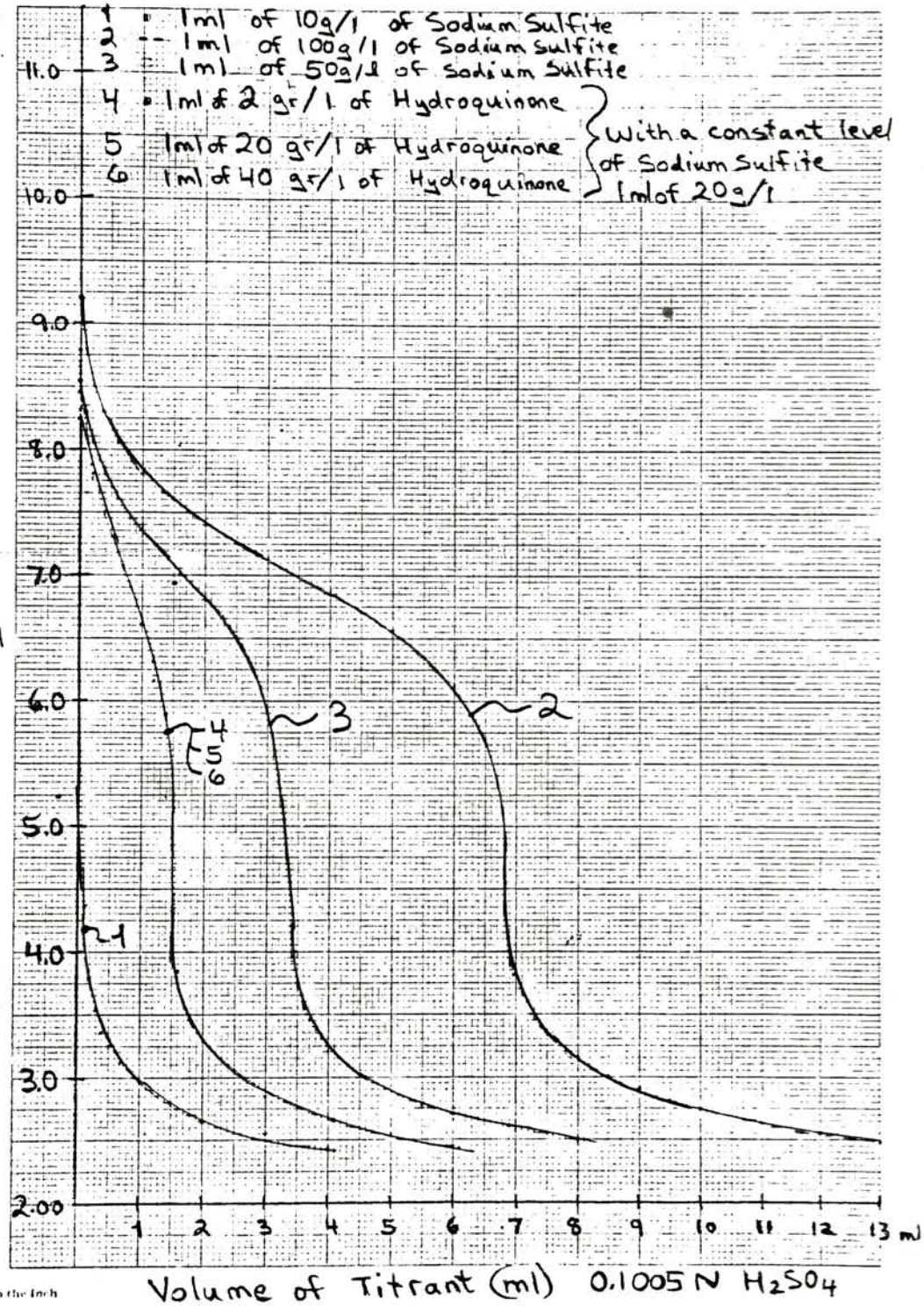
Sodium Sulfite with base titrant - Single Ingredient Concentration Series Buffer Curves (extended pH range)



20 Squares to the Inch

GRAPH 13

Hydroquinone - Single Ingredient Concentration Series Buffer Curves

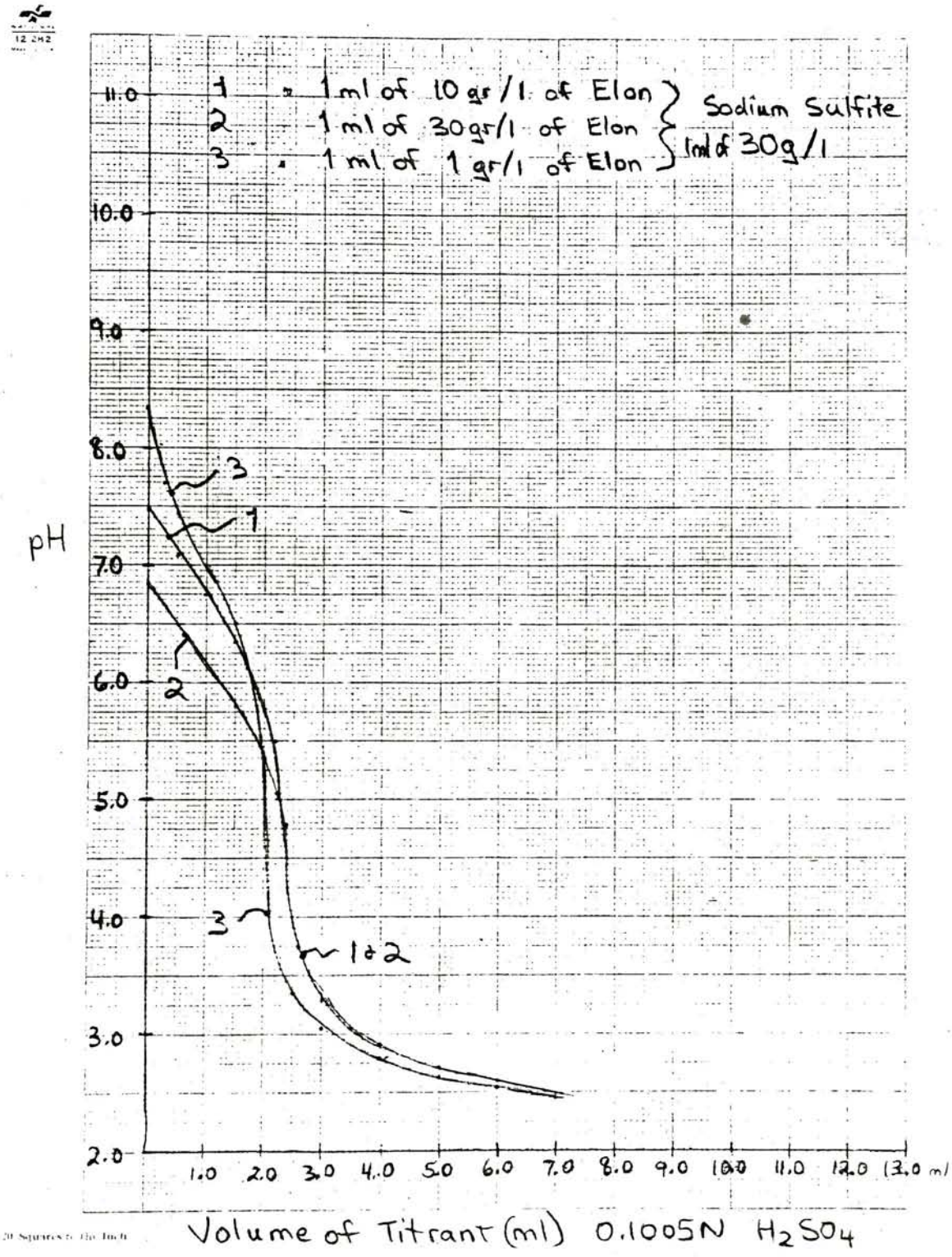


20 Squares to the Inch

GRAPH 14

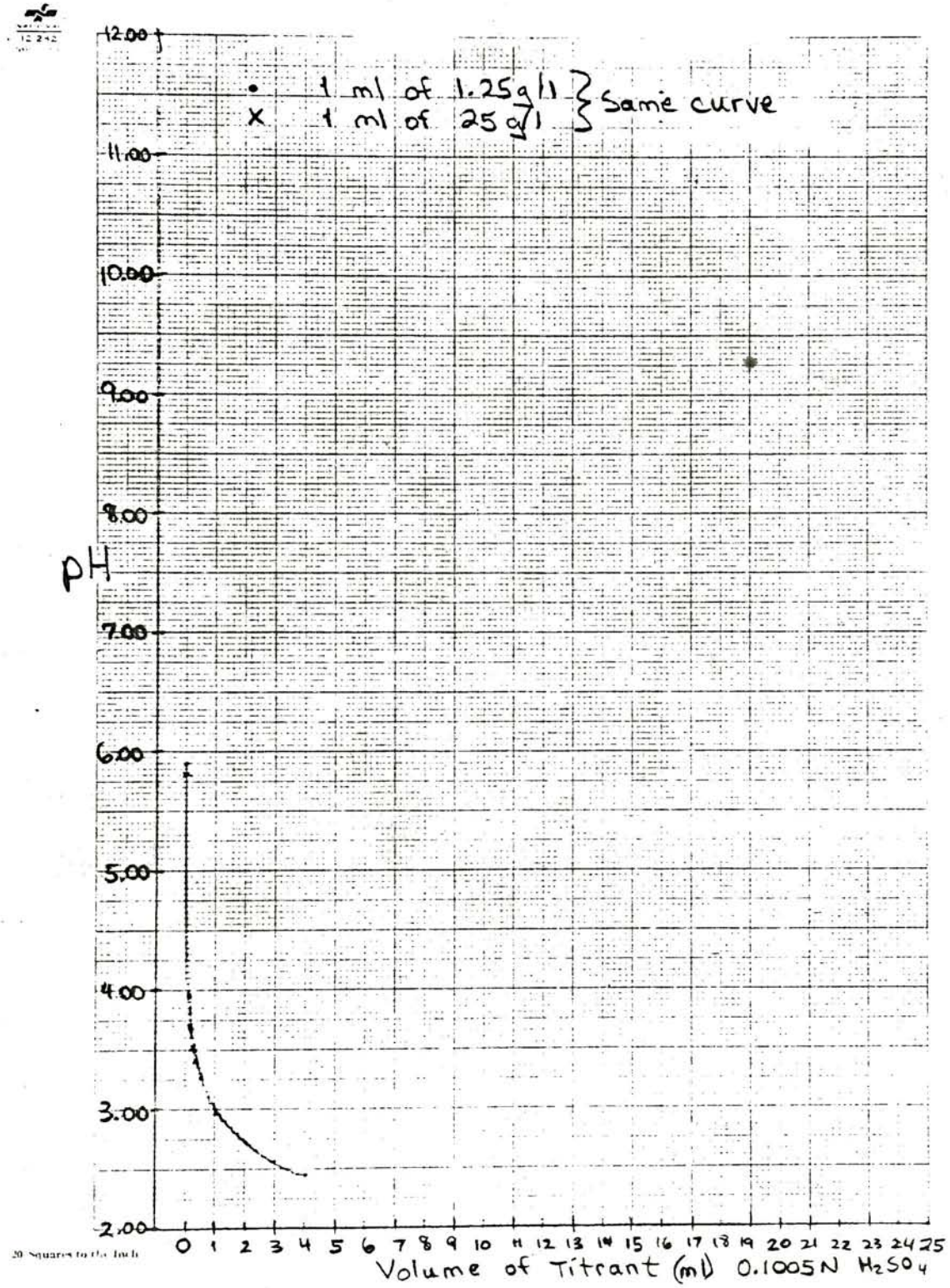
Elon -

Single Ingredient Concentration Series Buffer Curves



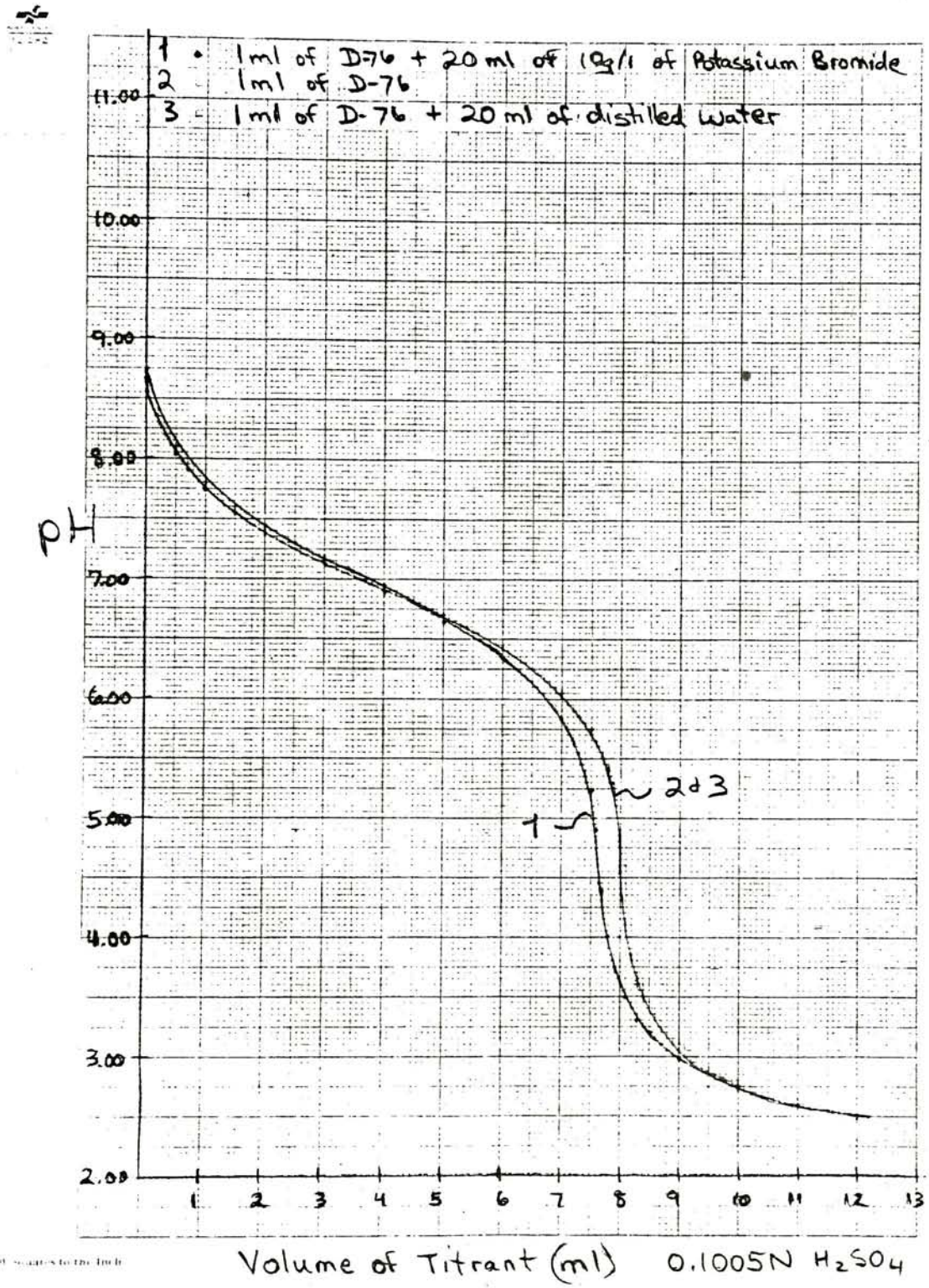
GRAPH 15a

Potassium Bromide -
Single Ingredient Concentration Series Buffer Curves



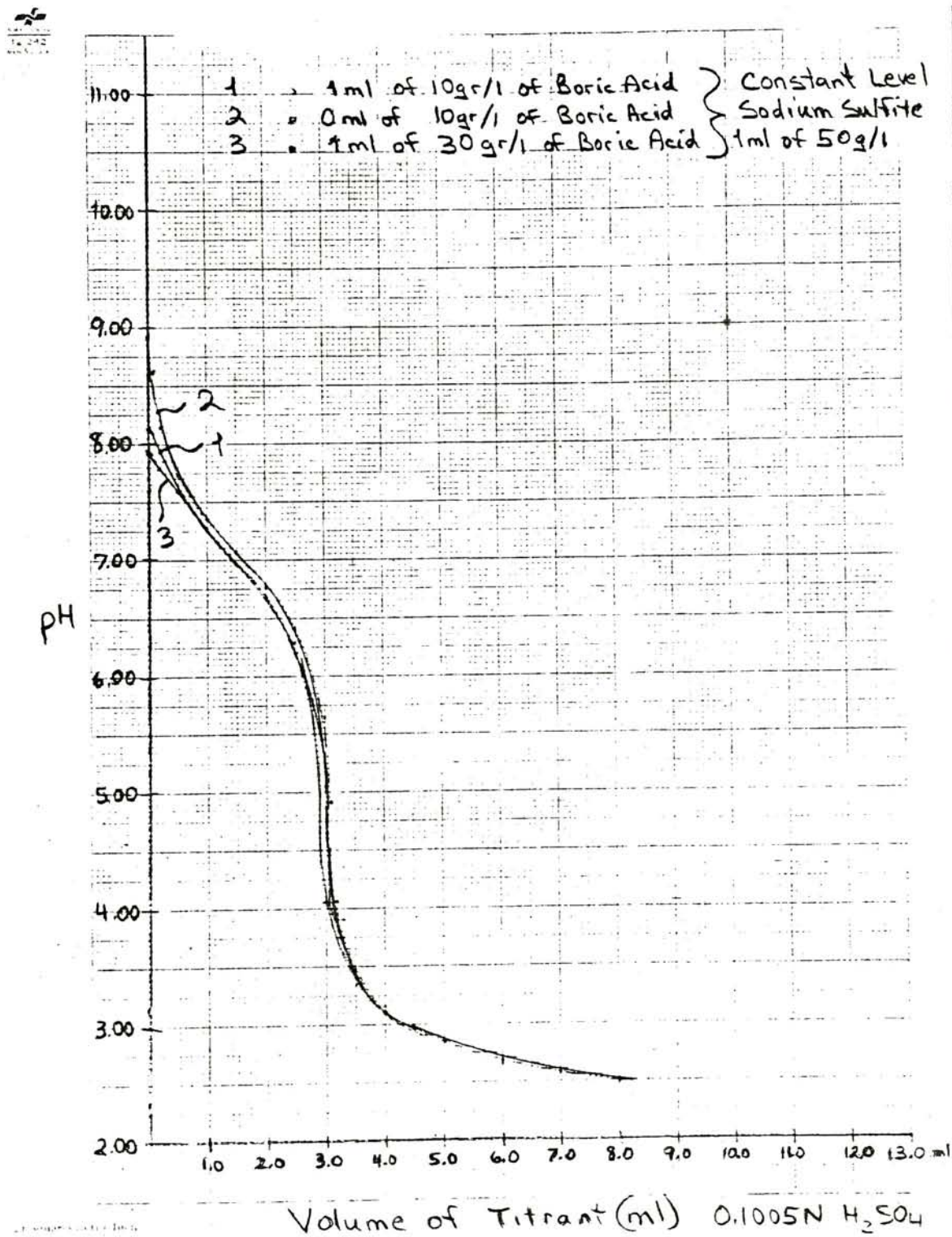
GRAPH 15b

D-76 with and without Potassium Bromide Added



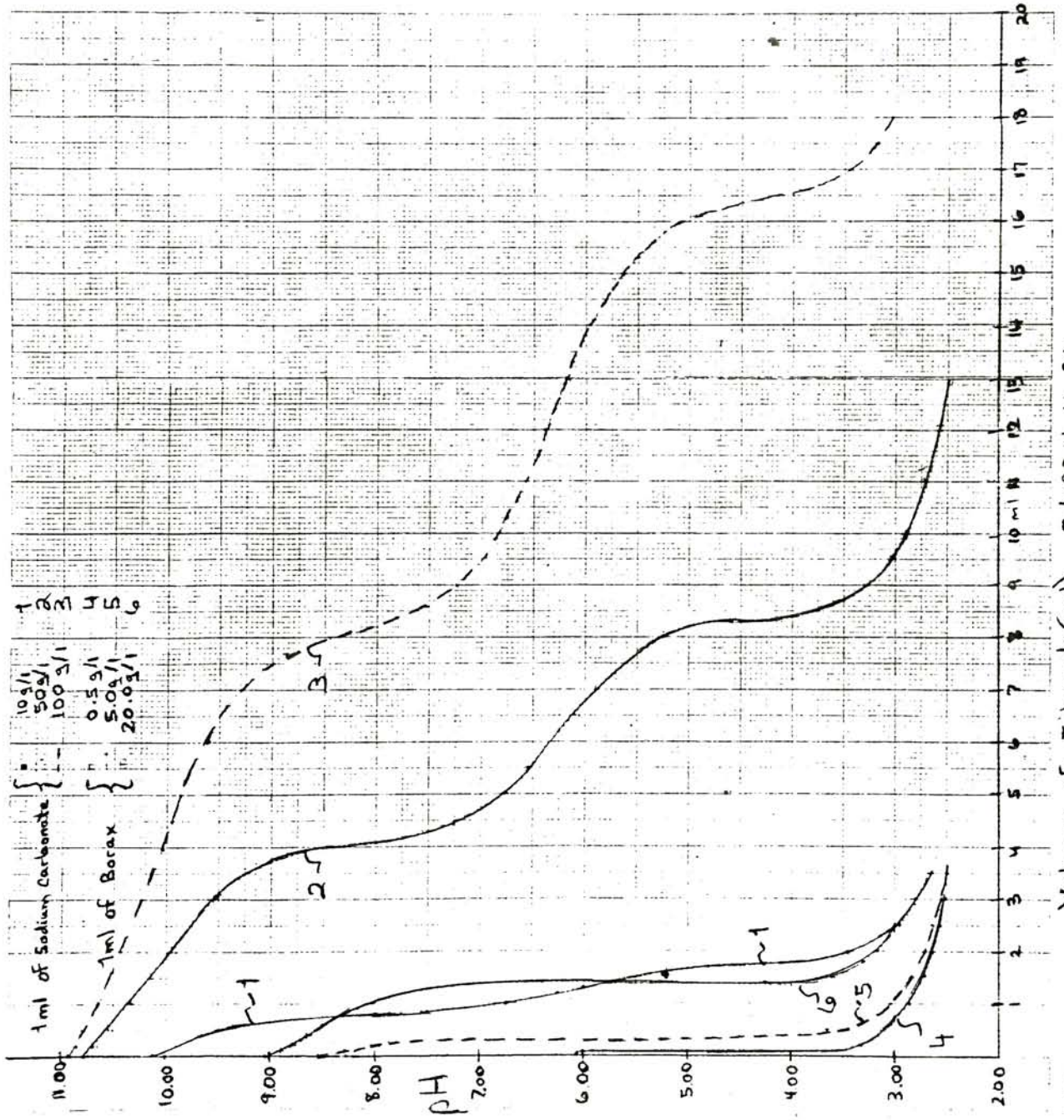
GRAPH 16

Boric Acid -
Single Ingredient Concentration Series Buffer Curves



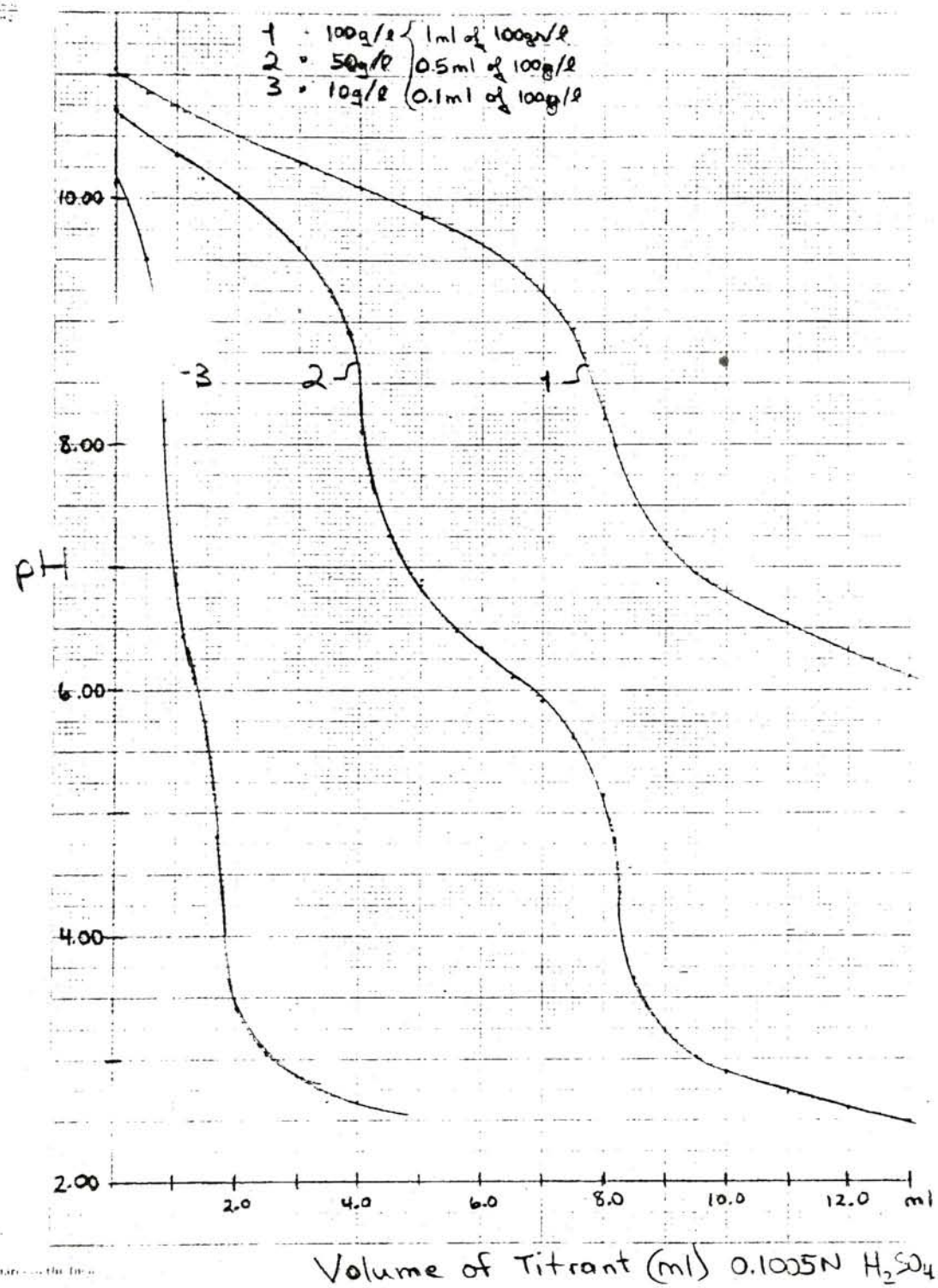
GRAPH 17

Borax and Sodium Carbonate -
Single Ingredient Concentration Series Buffer Curves for each ingredient



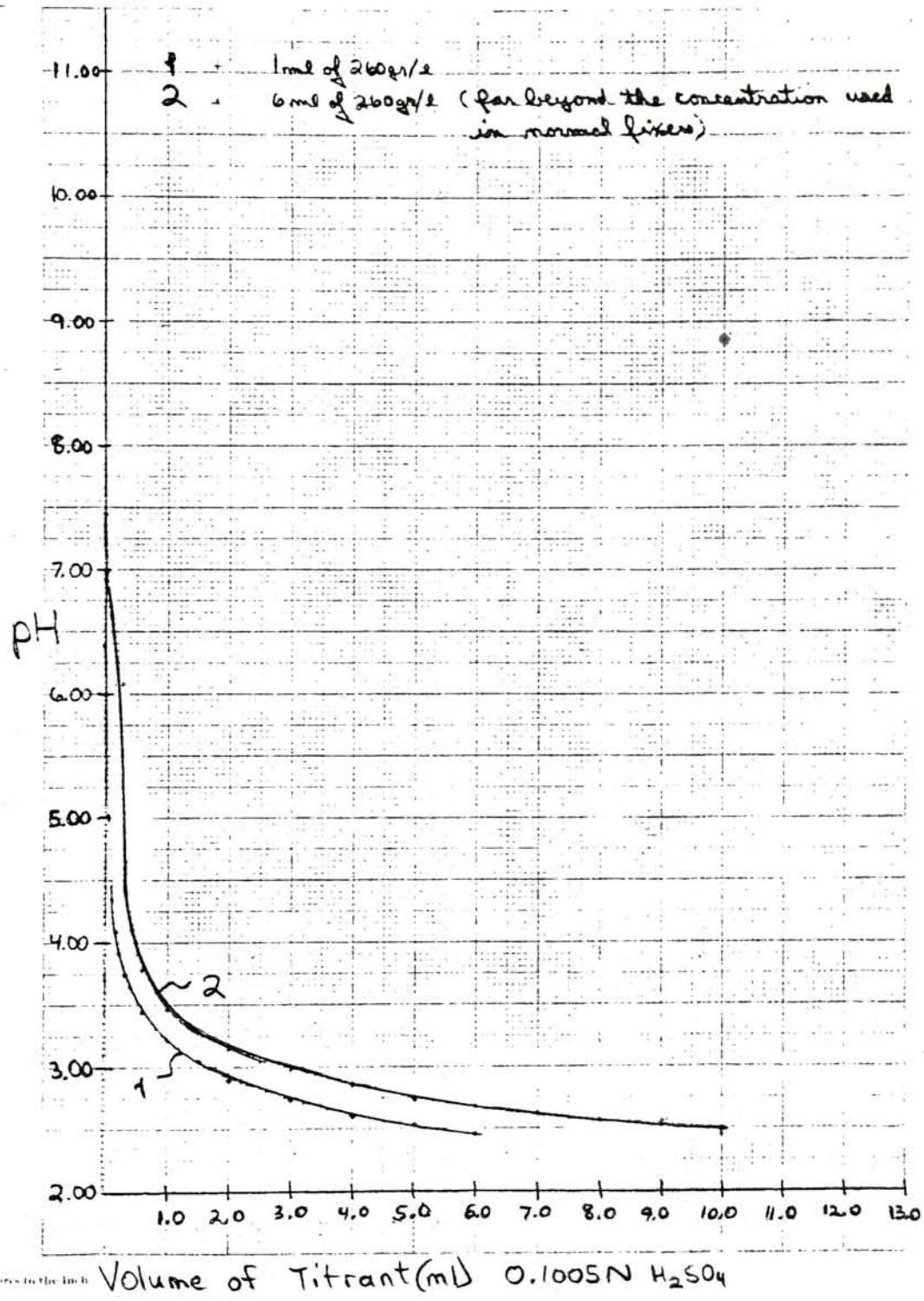
GRAPH 18

Sodium Carbonate -
Single Ingredient Concentration Series Buffer Curves



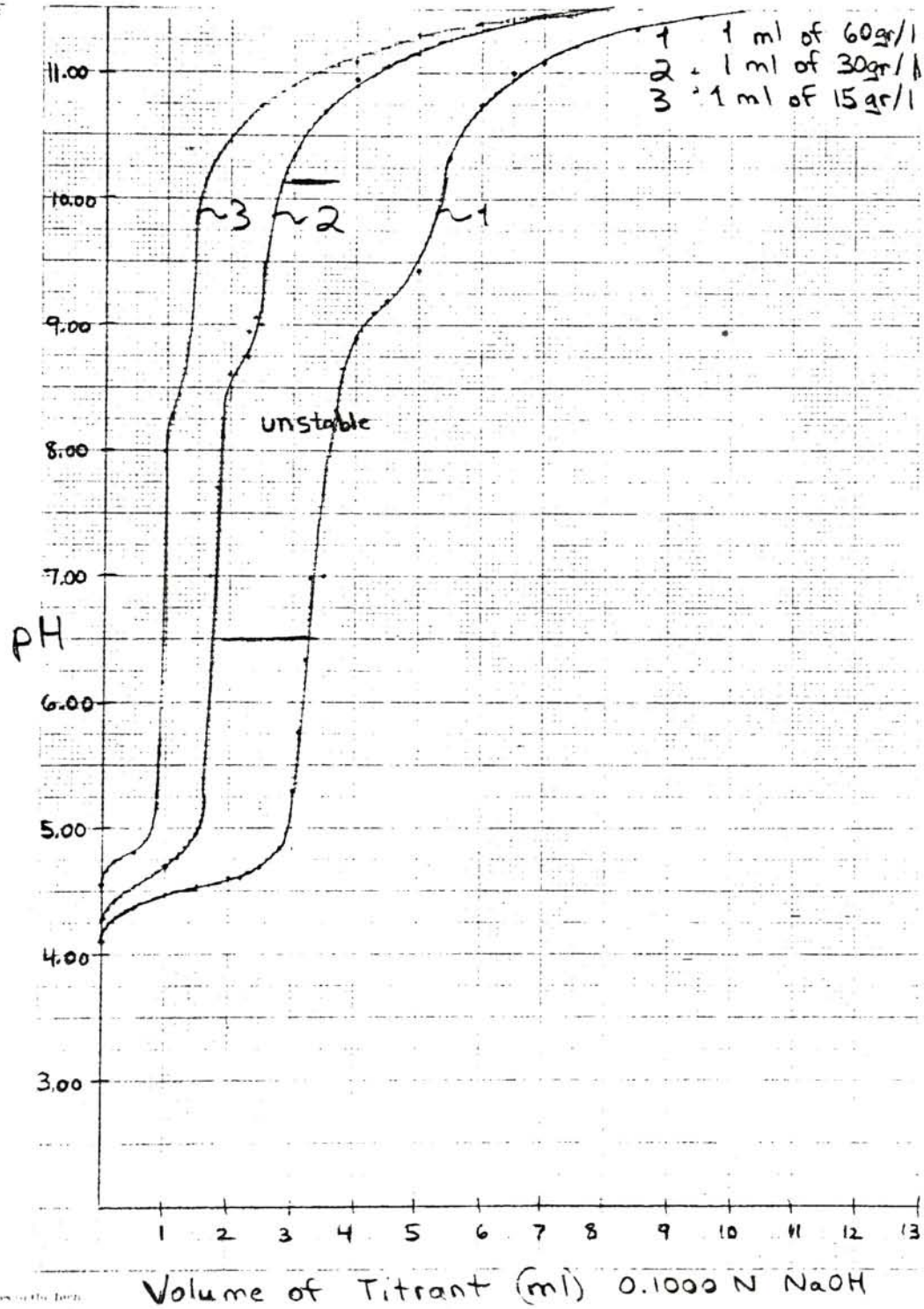
GRAPH 19

Sodium Thiosulfate -
Single Ingredient Concentration Series Buffer Curves



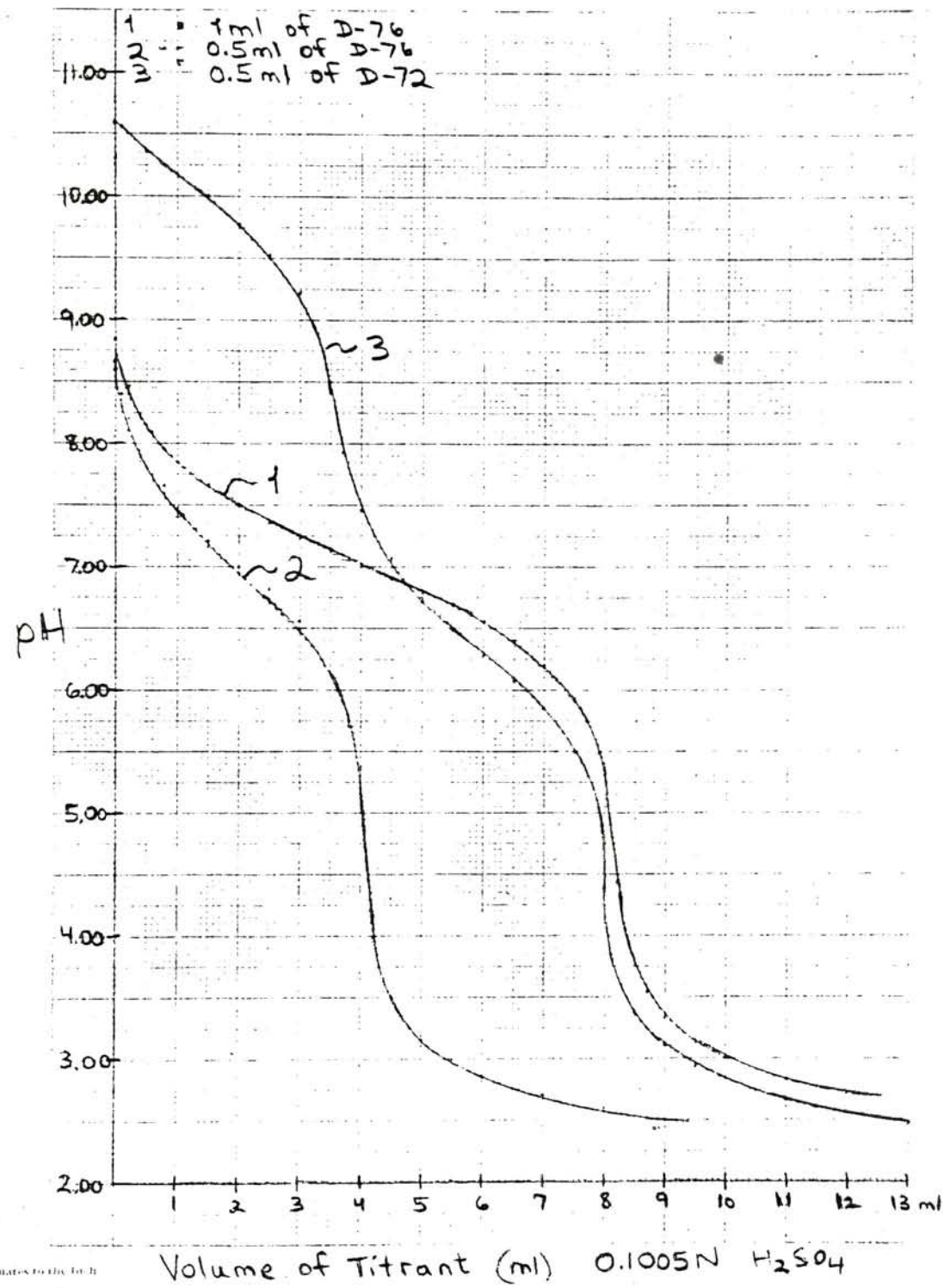
GRAPH 20

Potassium Alum -
Single Ingredient Concentration Series Buffer Curves



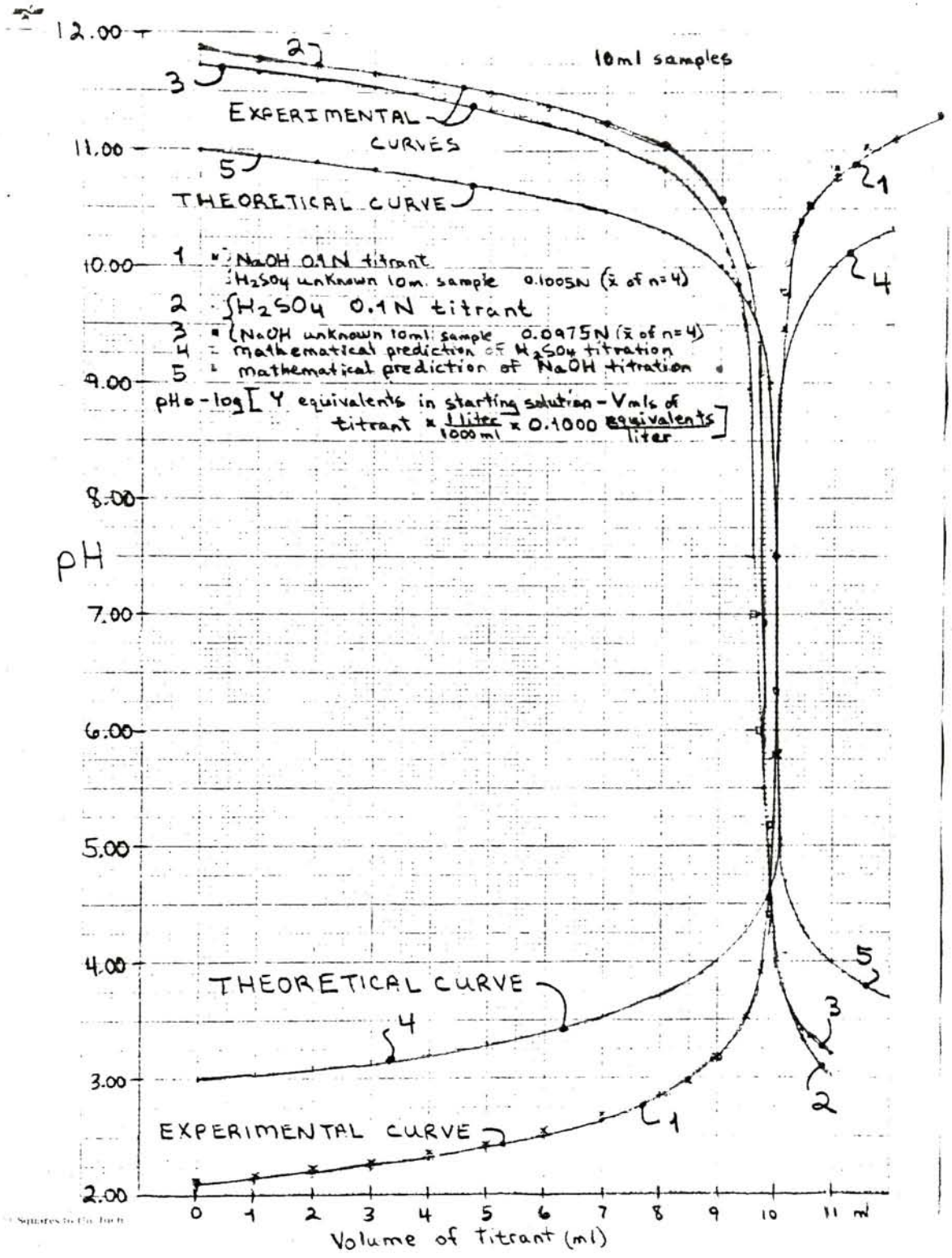
GRAPH 21

Kodak's D-76 and D-72 -
Buffer Curves



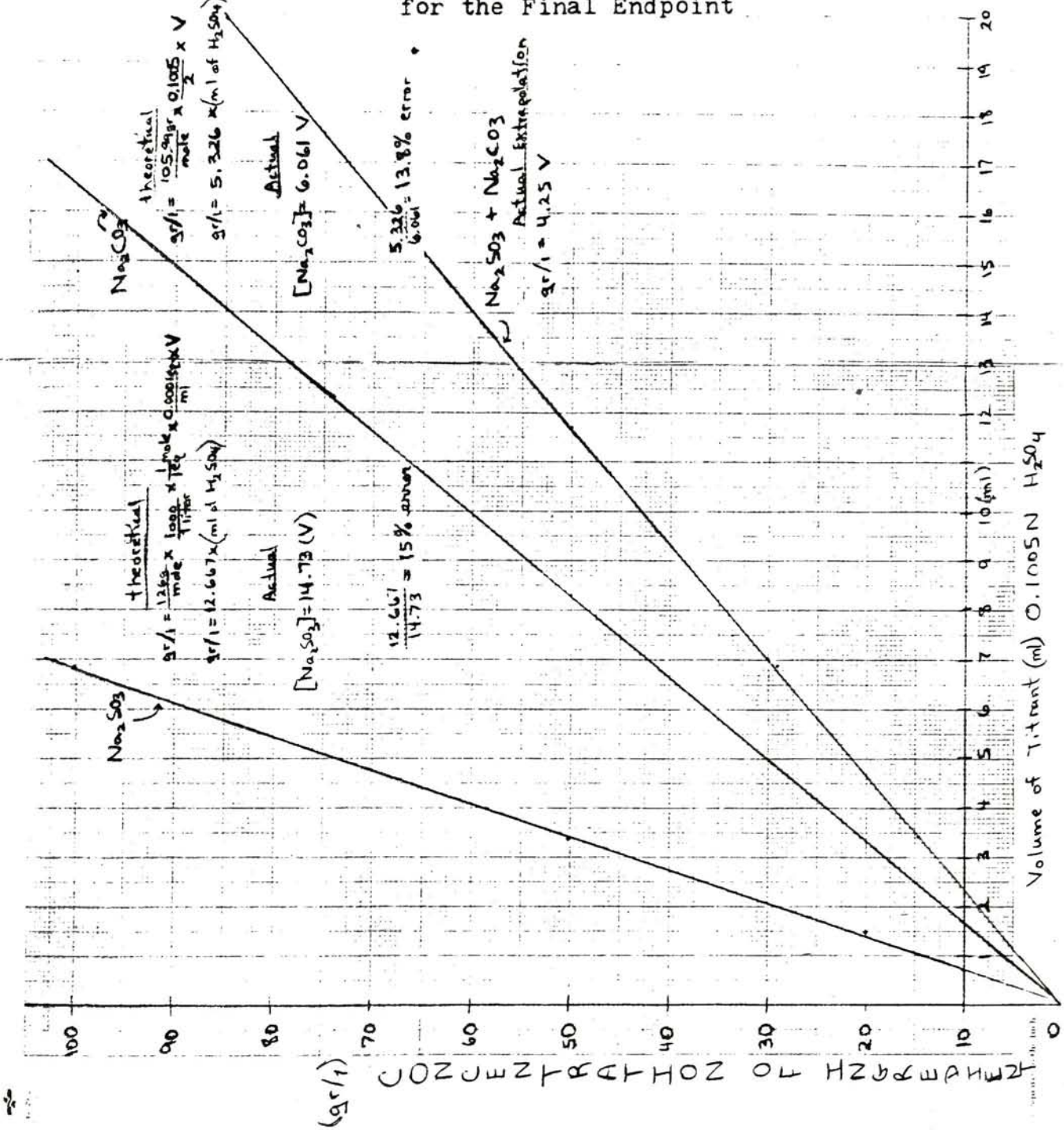
GRAPH 22

Titrant Standardization Buffer Curves



GRAPH 23

Ingredient Concentration vs. Volume of Titrant for the Final Endpoint



DISCUSSION

I. Automatic Titrator

a) Improvements to the system

Initially the automatic titrator took on the average of 16 minutes to titrate a sample by adding 35 ml. of titrant in 1 ml increments. However, the main advantage of the automatic titrator is to be able to submit a number of samples for titration at once. At this speed the sixteenth sample would be titrated four hours after the first titration, provided all of the samples required an average of 35 additions of titrant. In this time period, samples can reacte with the air. This can be seen in Graph 6 on p. 31. The curve number represents the order of the samples on the titrator. The graph shows a large variability between buffer curve 1 and 15. The last samples to be titrated show a buffer curve shifted to the left more than would be expected. Also when the experiments used hydroquinone with low concentrations of preservative, aerial oxidation was noticed before these samples were titrated. Thus, to decrease the error, the time per titration had to be decreased.

The algorithm was changed in many ways to increase the speed of the automatic titrator. The sum of these changes decreased the time per titration from 16 minutes to 6 minutes for the addition of 35 mls. of titrant. The speed increased by a factor of 2.5. Thus the sixteenth sample would be titrated only 1½ hours after the first titration, if all samples required 35 mls. of titrant. However runs do not require such large volumes of titrant to be added for each titration. If time is still a factor then the most

unstable samples could be titrated first or smaller runs could be used.

b) Testing the automatic titrator's environment and equipment

Since the pH is dependent on temperature, tests were run to monitor the temperature in the automatic titrator's environment (See Graph 1 on p. 26). Over a 24 hour period there are three major factors that determine the temperature of the titrator samples.

The building is an aluminum structure which absorbs the sun's radiation effectively. When the sun rises the laboratory temperature rises 4.5°C. Likewise when the building goes into shadow, the temperature significantly decreases.

The second factor that affects the temperature of the laboratory, is whether the door from the laboratory to the plant is opened or not. The laboratory is not heated so it must absorb heat from the floor and walls when the laboratory door is closed. With the door opened, the laboratory temperature is affected by the thermostat in the plant.

The third factor is the mixer motor. The temperature of the mixer motor increases the solution's temperature by 0.7°C over a six minute period of time.

The temperature should remain relatively constant during a run of a number of titrations to decrease the affect of temperature on high and low pH readings. It was found that the temperature is stable to $\pm\frac{1}{2}$°C between 12:00 and 18:00. The average temperature between these times is 22.0°C. With the laboratory door opened and the sun set, the temperature is 20 $\pm\frac{1}{2}$°C between 19:30 and 2:00.

These are the optimum times when the titrations should be run for a minimum of pH error.

The pH meter amplifier was also monitored for a 24 hour period (See Graph 2 on p. 27). The amplifier drift correlated 87% with the temperature of the laboratory. Thus, there is no major problem with amplifier drift outside of the temperature's influence.

After the titrant pump had been calibrated to a 5 ml. buret for a week, the pump accuracy and precision was tested under a number of conditions. The results have been tabulated on p. 24. When the titrant delivery tip is touching the measuring buret, there is capillary action to draw some of the solution out of the tip. The result was an 0.0331 increase in the standard deviation. With time the gravity pulls some of the solution down the hose and back into the titrant pump to decrease the volume delivered. When the pump is primed once before each test, there is an 0.049 ml. increase in the volume and an 0.0204 decrease in standard deviation. When a time lag is imposed between tests, there is more of a chance for the solution to drain into the titrant reservoir. In comparison to the tests with the pump primed, there was an 0.086 ml. decrease in the average volume measured when a time lag was imposed. To help eliminate the gravitational effects, the titrant pump, titrant reservoir and delivery tip were put at the same height. With the delivery tip suspended and the components at the same height, the best accuracy and precision were attained - average = 4.998 and standard deviation = 0.01084 for sample size of 6.

The accuracy and the precision of the titrant pump is more critical than a buret because the titrant pump error is cumulative

while the buret measurements can correct the error on the next addition of titrant. If the buret measurement is over or under the desired volume, the next addition of titrant can still deliver a correct total volume desired. If the titrant pump's average volume delivered is too larger or too small than the error will accumulate as each offset volume is delivered. However, with the titrant pump components at the same height and the delivery tip suspended, there will be a 99.7% chance that the volume of titrant delivered will be 34.986 ±0.033 mls. for an expected value of 35.000 mls.

To determine the effects of the initial volume of water on the buffer curves, this volume of water was varied. A 20 ml. increase in volume decreases the starting pH by about 0.05. The largest difference in pH due to a 20 ml. difference in the initial volume of water was 0.40 pH units at the activator's first endpoint (See Graph 3 on p. 28). If the initial volume is held to 75 ±2 ml., the pH should remain within 0.04 pH units.

c) Standard error of the automatic titrator vs. the manual titration

The automatic titrator's repeatability has proven to be better than the manual titrations. The automatic titrator's standard error was 0.0151 standard deviation units lower than the manual titrations. The response variable is pH. The resolution of the automatic titrator system depends on the ingredient because different ingredients are more sensitive to additions of an acid or a base. For sodium sulfite with a sample size of 3, there is a 95% chance that a 4.4 g/l or larger difference could be detected. With sodium

carbonate, there is a 95% chance of detecting a concentration of 1.8 g/l or larger when a sample size of 3 is used.

II. Evaluating the Buffer Curve Analysis

a) Monitoring the stability concentrated sample solutions

The tests were performed to resolve any change in the buffer curve characteristics of an ingredient due to the concentrated solutions' long periods of storage. Over a three week period when the solutions were used, the volume of air in the storage flasks increased, but the effects to the buffer curves were insignificant. The buffer curves labeled B and D in Graph 4 on p. 29, do not show a significant difference between the fresh and old solutions. These results were based on the concentrated solutions of sodium sulfite and sodium carbonate.

b) Limitations in the buffer curve analysis

The buffer curve analysis is subject to a few limitations. One limitation that applies to all ingredients can be expressed by the saying, "only the strong survive." Only those ingredients with concentrations that are close to the ingredient with the largest concentration may be detectable. In general, ingredients with concentrations greater than 1/10th of the largest concentration is detectable. This can be seen in the graphs of the factorial experiments (See Graphs 8 and 9 on pp. 33 and 34). The equivalents of titrant required to neutralize the largest concentration will determine the resolution of that analysis. If there is an ingredient that is 1/10th the equivalents of the largest ingredient, then the

volume of titrant would have to increase by a factor of 10 to get the same resolution as the largest ingredient. This is impractical for a titration using 30 mls. to form the buffer curve, because the volume of titrant would have to increase to 300 mls. The automatic titrator would take 1 hour to titrate the sample and the manual titration would take 4 hours.

A second important limitation of the buffer curve analysis is that some ingredients are not suited for this analysis. The concentrations typically used in photographic processing solutions are not detectable when an 0.1 N titrant is used. Some ingredients may not affect the pH at all. Such ingredients include potassium bromide, hydroquinone (See Graph 13 on p. 39), boric acid (See Graph 16 on p. 43), and Na_4EDTA (See Graph 5 on p. 30). Borax and elon are barely detectable at the concentrations typically used in photographic processing solutions (See Graph 17 on p. 44 and Graph 14 on p. 40, respectively). In the case of sodium thiosulfate, the ingredient doesn't resist the addition of an acid. Instead it converts into another compound without resisting the additions of titrant. With potassium alum, the rate of the reaction to reach equilibrium is slow. When the titrant is added, the pH changes quickly to put the chemical reaction in the forward direction, but it passes its equilibrium and slowly reactes in the reverse direction to reach its equilibrium. The rate of the reaction is slow in the reverse direction. Thus, the pH will not stabilize for a number of minutes after 1 ml. of titrant has been added. Such a titration may take an hour or so to do with a manual titration. This slow rate of reaction makes the buffer curve analysis undesirable for use with such ingredients as potassium alum.

The analysis has been able to resolve a number of ingredients used in photographic processing solutions. These ingredients include sodium sulfite, sodium carbonate, acetic acid, aluminum sulfate, sodium hydroxide, and potassium alum. These ingredients can be found in photographic developers, fixers, activators, or stabilizers.

There was no detectable change in the buffer curve with potassium bromide alone in a solution at concentrations much larger than is typically used in processing solutions (See Graph 15a on p. 41). It was also shown that these concentrations had an insignificant influence on the buffer curve when other ingredients were present. The five ingredients in D-76 were subjected to 20 mls. of a 10 g/l solution of potassium bromide without changing the pH by more than 0.02 after the first milliliter was added. The buffer curve for this solution showed a small change when compared to an unaltered sample of D-76. The small change was the result of an increase in potassium bromide concentration that is 40 times the concentrations normally used in photographic processing solutions.

From the 2^4 factorial experiment with the ingredients used in D-72 (See Graph 9 on p. 34), it was determined that only sodium sulfite and sodium carbonate were significant ingredients. These ingredients' concentrations significantly affect the buffer curve. A buffer curve was performed with these two significant ingredients at the concentrations used in Kodak's D-72. This buffer curve was compared with the buffer curve for the solution of D-72, which was one of Kodak's products (See Graph 4 on p. 29). The significant difference between buffer curves E and F may be explained by the grade, age, assay, and environment of the ingredients. This difference

can be up to 6 g/l of sodium carbonate or 12 g/l of sodium sulfite. This analysis has been designed to determine the constiuents of unknown solutions with any grade, age, or assay. However, it is not the purpose of this analysis to find the constiuent's concentration for the specific grade that the unknown solution's manufacturer uses. An equivalent solution is required to match its performance and not necessarily the exact concentrations and grades. Thus, this difference in ingredients is insignificant if the equivalent buffer curve gives equivalent performance in the field tests.

c) Further evaluations

The increasing of the pH range to include the pH above and below the sample's normal pH has a limitation with the titrants being used. If a specific volume of an acid titrant is added to a sample, the base titration will not return to the same starting pH in the same number of equivalents (See Graph 12b on p. 38). This will be discussed further below. However, if the shape is desired from the extended pH range, this method is an aid. The extended pH can show the number of endpoints to help identify ingredients easier, but it is not an accurate measure of the ingredients' concentrations.

d) Mathematical representation of the data

The single ingredient buffer curves demonstrated linearity between the concentration of the ingredient and the volume of titrant required to reach the final endpoint. This was shown for sodium sulfite and sodium carbonate (See Graph 12a on p. 37). This graph shows that doubling the concentration of sodium sulfite from 50 g/l

(Curve 2) to 100 g/l (Curve 3) will double the volume of titrant required to reach the final endpoint. This relationship is shown in Graph 23 on p. 50. However, when the theoretical relationship between a single ingredient's concentration and the volume of titrant required to reach the final endpoint was determined, there was as much as a 15% difference from the experimental relationship. In the case of sodium sulfite, the error could be from the starting pH. The starting pH of the single ingredient of sodium sulfite has already past its first endpoint. Thus one of the two species in sodium sulfite has been neutralized. The degree of neutralization is not known, but it is suspected that it is not fully neutralized because the theoretical relationship for sodium sulfite based on one equivalent per mole is too small and the relationship based on two equivalents per mole is too large as is shown on p. 24 in the Results section. Some other error may be introduced by the grade, age, and assay of the ingredients. This could explain the error found with sodium carbonate.

The relationship between the concentrations for more than one ingredient and the volume of titrant required to reach the final endpoint is not the sum of the individual ingredients (See Graph 4 on p. 29). The sum of the volumes of titrant required to reach the final endpoint for sodium sulfite (Curve B) and sodium carbonate (Curve D) is significantly larger than the volume of titrant for the buffer curve (Curve 4) whose solution contains the two ingredients together. This nonadditivity shows a distinct interaction between the two ingredients. Consequently, the relationship between the ingredients and the buffer curve becomes more complex. The

relationship between an ingredient's concentration and the volume of titrant required to reach the final endpoint depends on the other ingredients present in the solution.

The theoretical calculations of the buffer curves for the titrants were based on an assumption that the titrants dissociated 100%. The theoretical buffer curves had a lower pH than the actual buffer curves on the basic side of the pH scale and the theoretical curves had a higher pH than the actual buffer curves on the acid side of the pH scale (See Graph 22 on p. 49). This demonstrates that the titrants do not dissociate 100%, but in fact the titrants have some buffer qualities. This was also seen in the tests done on the extended pH range (See Graph 12a on p. 38), when the titrants' volumes did not match. The equal equivalents were in the solution, but since the titrants don't dissociate 100%, not all of the hydrogen ion added is free to neutralize 100%. This further adds to the complexity of the buffer curve.

The possibilities for representing the buffer curve with a mathematical model were investigated throughout the project. The major consideration in these curve fitting techniques is whether the data contains any interaction. If the data doesn't contain any significant interaction, then the job of equation fitting is greatly simplified. But, the presence of interaction in any of the data sets being fitted will required the model to include interaction. As the number of variables increase the combinations of interaction also increase. This makes the mathematical model quite complex due to all of the coefficients required. The laboratory work required to satisfy the mathematical model increases

exponentially with the number of ingredients, when interaction must be considered. The tests for linearity showed that there is interaction of ingredients in the buffer curves and thus a mathematical model of these curves must include interaction.

The mathematical model for a buffer curve with a strong acid and a strong base is a simple logarithmic function when they dissociate 100%. The buffer curve analysis would not deal with chemicals that always dissociate 100%. The solutions being analyzed contain ingredients which are in equilibrium and don't dissociate 100%. The titrants, themselves, do not dissociate 100%, but also are in equilibrium. This equilibrium adds to the complexity of the mathematical model. Furthermore, there are ingredients with more than one equilibrium constant. These polyacids or polybases will have more than one endpoint which can be seen for example in the buffer curves for sodium carbonate. Thus, the mathematical model has a number of complex contributions.

In the methods investigated, only the method of principal components could handle the interaction, but the amount of complexity with the increased number of ingredients, the increased laboratory work, and the different dissociation constants of the ingredients, would make this method of curve fitting difficult. More investigation should be done on this method of principal components and other curve fitting methods while taking into account the considerations listed above.

III. Summary

The determination of photographic processing solutions through buffer curve analysis has some merit. With the use of the automatic titrator system and the consideration of the analysis' limitations, the analysis can be useful in determining ingredients and their concentrations.

IV. Future Work

The work that has been done in this research project, has only begun to investigate the buffer curve analysis. The number of ingredients that were investigated was quite small. In the future, more ingredients should be investigated to obtain a better knowledge of which ingredients the analysis can detect and possibility demonstrate other limitations with this analysis.

The linearity and nonlinearity between ingredient concentrations and volume of titrant needed to reach the final endpoint has been seen for only two ingredients - sodium sulfite and sodium carbonate. More ingredients should be studied for a linear or nonlinear relationship at other points on the buffer curve besides the final endpoint. The interaction between ingredients should be studied further in an attempt to express the interaction mathematically. A quantitative measure of this interaction could render the analysis more useful and accurate. The interaction should be compared for different chemicals in hopes to explain better the source of the interaction so that a quantitative prediction could be made on the interaction of specific ingredients.

A model for the buffer curve should be further studied using

chemical, statistical, and mathematical theory. There are a number of problems to consider when equation fitting the buffer curve, some of which have been discussed above.

The automatic titration system is presently able to perform titrations, collect data, and store the data. The system could be greatly enhanced by creating a data library with an index that the computer can reference to when specific data is required to run manipulation programs. This would organize the system and allow for a more powerful use of the computer. More manipulation programs should be written to analyze the data.

The analysis has been directed towards the determination of unknown processing solutions. Perhaps the analysis could be more useful in the area of photographic processor control or as a confirmatory analysis after an ingredient has been isolated.

CONCLUSIONS

I. Automatic Titrator System

1) The improved automatic titrator system is 5 times faster than manual titrations.

2) The automatic titrator system is more accurate and precise than manual titrations.

3) The automatic titrator can perform 16 unassisted titrations; the system reads and stores the starting time, the starting solution temperature, the pH after each addition of titrant, the finishing time, and the finishing temperature; and the system can process the data by listing the values read, plotting the buffer curves, or compare the data sets.

II. Limitations of the Buffer Curve Analysis

1) The ingredients are not detectable by this analysis if their concentrations are much less than 1/10th the normality of the ingredient with the largest concentration that is detectable by the buffer curve analysis. The analysis is not sensitive enough without an impractical volume of titrant.

2) Some ingredients do not change the buffer curve when their concentrations are varied over a concentration range typically used for photographic processing solutions. This was demonstrated with potassium bromide, sodium thiosulfate, and hydroquinone.

3) Ingredients with slow rates of reaction will take an inconvenient amount of time to come to an equilibrium or stable pH. Potassium alum is an ingredient, which is undesirable to have in a solution when an acid-base titration is being performed because of its slow rate of reaction.

4) The analysis represents buffer curves for specific titrants and ingredients used in the titrations due to their specific chemical grade and assay.

5) There is linearity between the ingredient's concentration in a single ingredient solution and the volume of titrant required to reach the final end point, but this linearity fails when more than one ingredient is in a single solution due to interactions between ingredients. There is an interaction between ingredients that can be detected in the buffer curve.

6) The titrants do not dissociate 100%. The titrants form a buffer with the ingredients in the solution being titrated.

7) The resolution of the analysis depends on the specific ingredient's resistance to a change in pH. The greater this resistance is, the more sensitive the analysis can be to small differences in the ingredient's concentration.

III. Advantages of the Buffer Curve Analysis

1) There is a linearity between the concentration of an ingredient and the volume of titrant to the final endpoint with a single ingredient solution.

2) The analysis can detect a significant number of ingredients used in developers, activators, stabilizers, or fixers, when the titration equipment, grade of ingredients, and titrants are kept constant.

IV. Considerations for Representing the Buffer Curve with a Mathematical Model

The ingredients, their concentrations, the volume of titrant, the type of titrant, and interaction between ingredients effect the buffer curve and must be represented in the mathematical model.

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